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Contents

1. Introduction

This review focuses on the progress in the coordination chemistry of manganese for the calendar year 1996. It is based on a survey of Chemical Abstracts Volumes 123, 124 and 125. In addition, an independent search of pertinent journals has been made to ensure completeness.

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2. Manganese(VII)

Using a hydroxide flux a novel oxide $Na_4Mn_{0.5}P_{0.5}O_5$ compound, considered salt-like because of its ionic bonding and extremely hygroscopic nature, has been prepared [1]. It has been characterized by X-ray diffraction, IR spectroscopy and thermal analysis. Its structure comprises an $(Mn,P)O_4$ tetrahedral unit which is statistically composed of half MnO_4 and PO_4, the tetrahedra being held together by Na–O bonds thereby forming an ionic solid, $[Na_4O]^{2+}[(Mn_{0.5}P_{0.5})O_4]^{2-}$. In order to balance the charge in the empirical formula, Mn(VII) and P(V) centers must be present in equal amounts and they share the same crystallographic sites as evidenced from the crystal structure. The (Mn,P)–O bond distances are 1.59–1.61 Å in the tetrahedra and are thought to be largely covalent. The interaction between the two counterions via the Na–O connections is presumed to be mostly ionic with distances ranging from 2.31–2.70 Å.

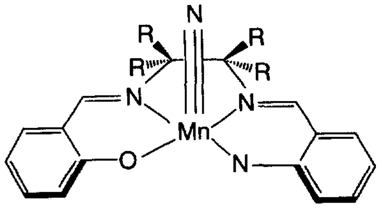
3. Manganese(V)

3.1. Complexes with oxygen and nitrogen donor ligands

The preparation of two novel nitridomanganese(V) salen-derived complexes which may be activated for nitrogen transfer with trifluoroacetic anhydride has been described [2]. Treatment of a methanolic suspension of $(salen)Mn^{III}Cl$ with NH_2OH and aqueous NaOCl generated (**1**) as green crystals. The compound was found to have a low solubility in most organic solvents thereby rendering its isolation and purification challenging. Circumvention of these problems was achieved by synthesis of a ligand in which the en backbone of salen was replaced with 2,3-diamino-2,3-dimethylbutane. This diamine was condensed with salicylaldehyde to generate the H_2saltmen, *N,N'*-(1,1,2,2-tetramethylethylene)bis-(salicylideneaminato) ligand as a yellow crystalline solid. A nitrido complex derived from this ligand was prepared by the reaction of $Mn(OAc)_2 \cdot 4H_2O$ with a solution of the ligand in methanol giving an air-oxidized intermediate. Subsequently this intermediate with NH_4OH and NaOCl generated (**2**). The latter was found to be remarkably stable to both air and water. Both complexes were characterized by ^1H and ^{13}C NMR spectroscopy. An MnN stretching frequency at 1047 cm^{-1} was obtained for both complexes indicating a triple bond. From X-ray crystallography, both compounds are monomeric and have an Mn–N bond length of 1.51 Å. Studies on the use of these compounds as nitrogen transfer reagents for enol ethers are described.

3.2. Complexes with nitrogen donor ligands

The synthesis and characterization of six-coordinate nitrido complexes including manganese has been achieved [3]. They were obtained from the photolysis of



R = H: (salen)Mn(N) (1)

R = Me: (saltmen)Mn(N) (2)

octahedral monoazido complexes $[LM^{III}(\text{didentate ligand})(N_3)]^{n+}(X^-)_n$ in the solid state or in solution yielding the corresponding six-coordinate complexes $[LM^{V}(\text{didentate ligand})(N)]^{n+}(X^-)_n$, L = 1,4,7-triazacyclononane or its *N*-methylated derivative, L′, the didentate ligands are acac, 2,2,6,6-tetramethylheptane-3,5-dionate, picolinate, phen and oxalate, and X^- is perchlorate or hexafluorophosphate. The structure of $[L'M^{V}(acac)(N)]BPh_4$ has been determined by single crystal X-ray crystallography with a very short Mn–N bond of 1.518(4) Å which is indicative of a triple bond. The Mn–O distances are 1.943(4) and 1.948(4) Å while the Mn–N distances are 2.055(5), 2.073(5) and 2.301(4) Å. The susceptibility of different samples of the complex has been measured in the range 2–300 K using a SQUID magnetometer and upon correction for underlying diamagnetism residual paramagnetism was found. The complexes were also characterized by EPR and electronic spectroscopies.

4. Manganese(IV)

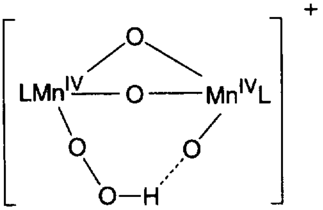
4.1. Complexes with oxygen donor ligands

A report has appeared describing the spectroscopic and magnetic properties of the first stable multiply protonated tetranuclear Mn(IV) complex $[Mn_4O_4(OH)_2(tacn)_4](CF_3SO_3)_6$, tacn = 1,4,7-triazacyclononane, which was formed by the successive protonation of the adamantane-like $\{Mn_4O_6\}^{4+}$ core [4]. The magnetic and structural outcome of protonation of the title complex were investigated using ^{1}H NMR spectroscopy. The complex was titrated with triflic acid in CD_3CN and was followed by ^{1}H NMR spectroscopy; this reveals that each protonated state is distinct with no observable degradation products. The observation of distinct spectra is due to slow rates of proton self-exchange on the NMR time scale. Values of μ_{eff} 4.36 μ_B for the unprotonated and monoprotonated and 3.14 μ_{eff} for the diprotonated species at 22 °C are a reflection of the change in overall coupling from ferromagnetic to moderately antiferromagnetic.

The synthesis, X-ray structure and magnetochemical properties of an Mn_{13} complex which displays a novel supercubane structure $[Mn^{IV}Mn^{III}_6Mn^{II}_6$

$(\mu_5\text{-O})_6(\mu_3\text{-O})_2(\mu_3\text{-OEt})_6]^{12+}$ core has been reported [5]. It was prepared by adding a 25 wt% solution of $[Me_4N]OH$ in methanol solution dropwise to a methanol–THF solution (1:1) of $Mn(O_2CPh)_2 \cdot 2H_2O$ and 2,2′-biphenol. After stirring for 10 min the resultant solution was heated to boiling for 1 h. Subsequent evaporation to dryness, followed by washing with methanol gave a red-brown crystalline product. Crystals of the title compound were obtained by dissolving some of the product in THF/EtOH and layering this solution with CH_2Cl_2. From X-ray crystallography studies the 13 manganese atoms are six-coordinate with six oxygen ligands. Each of the 12 benzoate ligands symmetrically bridges between two Mn ions. The presence of a $\mu_5\text{-O}^{2-}$ moiety and the spontaneous formation of a molecule in which three different oxidation states of manganese exist are very rare events. The core is structurally similar to a piece of cubic metal oxide extended lattice. For this reason variable temperature (2–320 K) magnetic susceptibility data were collected for a polycrystalline sample in a 10.0 kG DC magnetic field employing a SQUID susceptometer. The value of μ_{eff} increases with decreasing temperatures from 18.6 μ_B at 320 K to a maximum of 18.9 μ_B at ~180 K below which μ_{eff} decreases to become eventually 9.05 μ_B at 2.00 K. An $S=15/2$ ground state was found for the complex which is explicable in terms of two interpenetrating spin sublattices.

The dinuclear complex $[Mn_2O_3L_2][PF_6]_2$ where L = 1,4,7-trimethyl-1,4,7-triazacyclononane was found to exhibit high activity for the formation of 8-hydroxy-2′-deoxyguanosine in the presence of hydrogen peroxide and 2′-deoxyguanosine [6]. The active species is postulated to be the unidentate peroxide adduct (**3**).



(3)

Electron spin resonance and electrospray ionization mass spectroscopic studies of the interaction of alkali and alkaline earth cations with manganese bis(μ-oxo) dimers have been carried out [7]. At the outset of the studies it was postulated that the placement of a Ca^{2+} ion in close proximity to a mixed-valent Mn_2O_2 core may cause a perturbation which would result in the appearance of a multiline-type ESR spectrum. The dimer $[(3,3'\text{-17-crown-6-SALPN})Mn^{IV}(\mu\text{-O})]_2$ was prepared in order to test this hypothesis. The reaction of (3,3′-17-crown-6-SALPN)Mn(II) with oxygen in acetonitrile generated the title compound. The dimer was then reacted with two molar equivalents of $NaPF_6$, KPF_6, $CaTf_2$ or $BaTf_2$, (Tf^- in $SO_3CF_3^-$) to give complexes dimer · $2NaPF_6$, dimer · $2KPF_6$, dimer · $2CaTf_2$, dimer · $2CaTf_2$ or dimer · $2BaTf_2$, respectively. Reduction of the dimers to a mixed-valent state either chemically using Cp_2Co or electrochemically was achieved and ESR studies were carried out. The ESR spectra comprised a 16-line pattern indicative of a valence trapped antiferromagnetically coupled species. Using ES-MS the cation containing Mn^{IV}, Mn^{IV} bis(μ-oxo) dimers were analyzed in methylene chloride and acetonitrile. Singly charged cations resulting from loss of an anion from the parent complex were observed in addition to ions in which cation exchange had occurred.

4.2. Complexes with oxygen and nitrogen donor ligands

A new type of manganese complex which facilitates the catalytic epoxidation of water-soluble olefins in an aqueous medium under mild conditions using hydrogen peroxide as oxidant has been obtained [8]. The complex $[Mn^{IV}(Me_3TACN)(OMe)_3](PF_6)$ where $Me_3TACN = N,N',N''$-trimethyl-1,4,7-triazacyclononane was synthesized from the reaction of $MnCl_2$ with Me_3TACN in methanol using Na_2O_2 as a strong base and an oxidizing agent. A red/brown crystalline hexafluorophosphate salt was obtained by crystallization from a methanol/water solution. From X-ray crystallography an octahedral Mn(IV) atom is evident with an N_3O_3 ligand environment. The Me_3TACN ligand is facially coordinated and the average Mn–N and Mn–O distances are 2.116(5) and 1.797(5) Å, respectively. Solution magnetic susceptibility measurements gave a measurement of 3.84 μ_B. The X-band EPR revealed two broad resonances at $g = 2.0$ and 3.6. Further characterization by UV–vis, FAB-MS and electrochemistry was carried out. Catalytic studies with olefins indicated a 12-fold rate enhancement with 1 mol% versus that with oxidant alone. Furthermore the stability of the complex was validated by repeated additions of olefin and oxidant.

The synthesis and structural investigation of a water-bound manganese complex obtained by cerium(IV) oxidation has been carried out [9]. The complex $[Mn_3O_4(phen)_4(H_2O)_2](NO_3)_4 \cdot 2.5H_2O$ was obtained from Ce(IV) oxidation of a concentrated solution of Mn(II) acetate and phen in 1.6N nitric acid. In this complex the manganese atoms occupy the vertices of an isosceles triangle, one of the manganese atoms is linked to the other two by two μ-oxo bridges. The latter two manganese atoms are themselves linked to each other by two mutual μ-oxo bridges. The Mn–Mn distances are 3.249 Å and 2.675 Å and the geometry about each Mn atom is octahedral. The average Mn–N distance is 2.065 Å while the $Mn–N_{oxo}$ distance is 1.798 Å. The complex is soluble in highly polar solvents such as water, DMF and DMSO, while it is insoluble in moderately polar solvents such as dichloromethane, chloroform and acetonitrile. It was further characterized by electronic and EPR spectroscopy, the EPR spectrum in powder form at 298 K exhibits a strong signal at $g \approx 2$. Upon lowering the temperature to 150 K, additional low-field lines were also observed. The frozen-solution EPR spectrum in DMF glass at 150 K reveals the multiline pattern which typifies $Mn^{III}Mn^{IV}$ species together with signals due to Mn^{II} signifying the decomposition of the trinuclear core. This study demonstrates the stabilization of coordinated aqua molecules in a high-valent Mn environment and suggests that the pH of the medium exerts a definite influence on the nuclearity and oxidation state of the manganese species formed.

Using the boronato ligand RBO_2^{2-} a new structural model for manganese-containing metalloproteins has been obtained [10]. When 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and phenylboronic acid were treated with $Mn(ClO_4)_2 \cdot 6H_2O$ in acetone in the presence of air yielded green crystals of complex $[LMn^{III}(Ph_2B_2O_3)(ClO_4)]$ whose structure comprises a monodentate ClO_4^- ion, a cyclic triamine and the didentate $[Ph_2B_2O_3]^{2-}$ anion as ligands. Hydrolysis of this complex in the presence of air in a mixture of ethanol/water/acetone (3:1:2) to which $NaClO_4$ was added resulted in red crystals of $[L_2Mn_2^{IV}(\mu\text{-}O)(\mu\text{-}Ph_2BO_2)_2](ClO_4) \cdot 2Me_2CO$ after two to three days. An X-ray crystallography study shows both Mn atoms to be in an octahedral environment and they are linked by two *syn,syn-O,O′*-coordinated phenylboronic acid dianions and a bent oxo bridge. A hydroxo mixed- valent $Mn^{II}Mn^{III}$ complex was obtained $[LMn_2^{II}(\mu\text{-}OH)(\mu\text{-}(CH_3)_3CCO_2)_2Mn^{III}L(ClO_4)_2]$ in which the valences are localized. Oxidation of the former by O_2 in a basic medium yielded red-violet crystals of $[LMn_2^{III}(\mu\text{-}O)(\mu\text{-}(CH_3)_3CCO_2)](ClO_4)_2$ in which the two manganese ions are linked by an oxo bridge. Magnetic susceptibility measurements were carried out for all four complexes, XANES experiments show that the Mn K-edge energy increases linearly with increasing oxidation level.

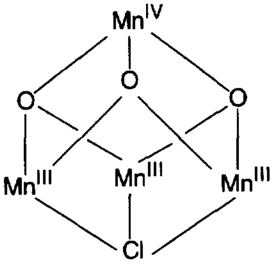
5. Manganese(III)

5.1. Complexes with oxygen donor ligands

A tetranuclear manganese carboxylate cluster $(N^nBu_4)[Mn_4O_3(O_2CPh)_9(H_2O)]$ was obtained in high yield from the reaction of $Mn(O_2CPh)_2 \cdot 2H_2O$ and $PhCO_2H$ in EtOH/MeCN with $N^nBu_4MnO_4$ [11]. Its crystal structure reveals that the anion comprises a $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ core in which the Mn^{III} centers are in a butterfly arrangement. Seven $PhCO_2^-$ are bridging while another $PhCO_2^-$ group chelates at one wingtip Mn atom with a terminal $PhCO_2^-$ and a water ligand at the other wingtip. This "naked" complex with only carboxylate and water peripheral ligation is an excellent precursor to other $[Mn_4O_2]^{8+}$ species. Treatment of the aforementioned complex with 2,2-diethylmalonate, Et_2mal, led to the octanuclear species $(N^nBu_4)_2[Mn_8O_4(O_2CPh)_{12}(Et_2mal)(H_2O)_2]$, a mixed-valence species containing two Mn^{II} and six Mn^{III} in an arrangement comprising of two butterfly $[Mn_4O_2]^{7+}$ units which are linked together by one of the $\mu_3\text{-}O^{2-}$ ions in each bridging unit thus converting to a μ_4-mode. Magnetic studies have been carried out.

The development of a new type of $[Mn_4O_3Cl]^{6+}$ complex containing oxygen only peripheral ligation, namely carboxylate and dibenzoylmethane groups (**4**), has been reported [12]. This mode of ligation has demonstrated reversible redox chemistry for oxidation and reduction which has not been seen for other complexes in this family. Substitution of Br^- by Cl^- has been carried out as a probe of the effect of this substitution in the water oxidation center.

Single-molecule magnet behavior for manganese distorted-cubane complexes has been demonstrated [13]; the complexes $[Mn_4O_3Cl_4(O_2CMe)_3(py)_3]$, $[Mn_4O_3Cl(O_2CMe)_3(dbm)_3]$,$[Mn_4O_3F(O_2CMe)_3(dbm)_3]$,$[Mn_4O_3(N_3)(O_2CMe)_3(dbm)_3]$,



(4)

$[Mn_4O_3(NCO)(O_2CMe)_3(dbm)_3]$ and $[Mn_4O_3(OC(O)Me)(O_2CMe)_3(dbm)_3]$ where dbm is the anion of dibenzyoylmethane. The central $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)]^{6+}$ distorted core has the Mn^{IV} ion at its apex, a μ_3-X^- ion bridging the basal plane and μ_3-O^{2-} ions bridging each of the remaining faces. Alternating current magnetic susceptibility data is presented for these complexes. Each complex exhibits a well isolated $S = 9/2$ ground state; zero-field splitting (ZFS) in the ground states with an axial field ZFS parameter D in the range -0.27 to $-0.38\ cm^{-1}$. An out-of-phase AC magnetic susceptibility signal is observed for these complexes which points to slow magnetization relaxation and indicates that individual molecules are acting as magnets.

The synthesis and characterization of dimanganese complexes derived from the divacant lacunary species $\gamma\text{-}[(SiO_4)W_{10}O_{32}]^{8-}$ has been reported [14]. Using the appropriate mixtures of Mn^{II} and MnO_4^- gave rise to the complexes, and the crystal structure of $[(CH_3)_3(C_6H_5)N]_4[(SiO_4)W_{10}Mn_2^{III}O_{36}H_6]\cdot 2CH_3CN\cdot H_2O$ was determined. The structure comprises one ordered polyanion $[(SiO_4)W_{10}Mn_2O_{36}]^{m-}$ in each asymmetric unit which represents the γ-isomer in which two adjacent edge-shared WO_6 octahedra have been replaced by MnO_6 octahedra. The adjacent Mn atoms are separated by a distance of 2.93 Å. Four $[(CH_3)_3PhN]^+$ cations, two acetonitrile and one water molecule were located with each polyanion. Magnetic susceptibility of this complex was measured between 2 and 300 K and indicate that the two Mn atoms are antiferromagnetically coupled, $J = -17.0\ cm^{-1}$ and $g = 1.965$. Electrochemical studies were conducted and reveal that the anion can be oxidized and reduced to Mn^{III}, Mn^{IV} and Mn_2^{II}, respectively.

The preparation, crystal structure and magnetic behavior of a new manganese dimer $[Mn_2(\mu\text{-}OCH_3)_2(sal)_2(CH_3OH)_4]$ has been reported [15]. The dimer is bridged by two μ-OCH_3 anions at an Mn...Mn separation of 3.00 Å. Each Mn atom is six coordinate and is further surrounded by a terminal didentate salicyclate ligand in an equatorial position while the axial sites are occupied by methanol ligands. This arrangement of ligands gives rise to a dimer with C_i symmetry with a crystallographically imposed center of inversion. The equatorial Mn–O distances are in the range 1.854(5)–1.928(6) Å while the axial distances are considerably longer — 2.259(4) and 2.259(4) Å — and are a reflection of Jahn–Teller elongation. Magnetic susceptibility measurements over the temperature range 80–300 K have been obtained and reveal an antiferromagnetic spin-exchange interaction between the atoms.

The preparation of a new heteropolytoxofluorotungstate anion $[MnW_{11}O_{37}F_3H]^{7-}$ has been reported [16]. It was characterized by FAB MS, IR and visible spectroscopy, CV and X-ray powder diffraction and deduced to have a Keggin structure in which the Mn atom is in an octahedral environment.

A successful method to prepare mixed metal polymanganese complexes using $K_2Cr_2O_7$ as an oxidation agent has been reported [17]. The reaction of the oxidation agent with $Mn(OAc)_2$ in CH_3CO_2H/H_2O mixed solvent generated $[Mn_{11}CrO_{12}(CH_3CO_2)_{16}(H_2O)_4]\cdot 4H_2O$ whose crystal structure was obtained. The dodecanuclear molecule comprises 12 metal atoms which are linked by triply bridging oxo-O atoms and carboxylates from acetate anions. The Mn–O distances are in the range 1.857(3) to 2.247(3) Å.

5.2. *Complexes with oxygen and nitrogen donor ligands*

Mixed-valence Mn^{III} complexes and a homo-valent Mn^{II} trinuclear complex have been synthesized [18]. The mixed-valent complex $Mn^{III}Mn^{II}Mn^{III}(hsaladhp)_2(AcO)_2(5\text{-Cl-Sal})_2(THF)_2$, $H_3saladhp$ = 1,3-dihydroxy-2-methyl(salicylideneamino)-propane, 5-Cl-Sal = 5-chlorosalicyclic acid, is the first example of a structurally characterized mixed-valent trimer in which the sixth position of the terminal manganese atoms contains a neutral ligand without an –OH group. Magnetic data incorporating a mean field correction were used in the interpretation of inter and intra-H-bond networks. The ESR signals for these mixed-valent compounds showed a multiline signal at low temperatures while a solid state study shows a temperature-dependent population interconversion for the low-field signal.

The coordination chemistry of the (4,5-dichloro-*o*-phenylene)bis(oxamato), Cl_2opba ligand with metals including manganese to obtain heterodimetallic complexes has been explored [19]. The manganese derivative $(N^nBu_4)_5[Mn(Cl_2opba)(DMSO)_2]_4$ was obtained. Its crystal structure reveals that the metal site is randomly occupied by Mn(III) and Mn(II) in 3/4 and 1/4 ratios, respectively. The Mn atom is in an elongated octahedral environment with two nitrogen and oxygen atoms of the oxamate ligand occupying the equatorial positions with mean Mn–N distances of 1.95 Å and mean Mn–O distances of 1.98 Å. The anionic $[Mn(Cl_2opba)(DMSO)_2]^{4/5-}$ are well separated with the shortest Mn...Mn intermolecular distance being 8.77 Å. The dimetallic complex $Cu(en)_2[Mn(Cl_2opba)(H_2O)_2]_2\cdot 2DMSO$ comprises centrosymmetrical $Mn^{III}Cu^{II}Mn^{III}$ trinuclear units with Cu–O–Mn bridges and uncoordinated DMSO molecules. The Mn(III) atoms are in a distorted octahedral environment. The mean Mn–N distance is 1.918 Å and Mn–O is 1.966 Å. Two water molecules occupy the apical positions at a distance (average) 2.250 Å. Intramolecular Cu...Mn and Mn... Mn separations are 3.836(1) and 7.671(2) Å. These complexes have been subjected to magnetic studies.

The synthesis, structure and magnetic susceptibility of the hydroxo-bridged complex $\{[Mn(TPP)]_2(OH)\}ClO_4$ have been described [20]. Its structure comprises two Mn(III) ions bridged by a single hydroxo ligand with an Mn–O(H)–Mn bridge angle of 160° and nearly coplanar porphyrin rings. The average Mn–O distance is

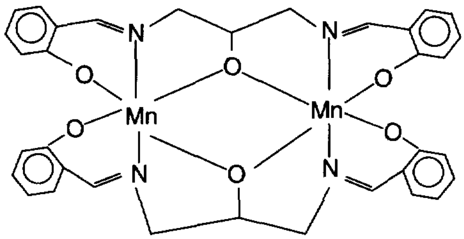
2.026(1) Å while the average Mn–N(porphyrin) distance is 2.008(7) Å and the Mn...Mn separation is 3.993 Å. Temperature-dependent magnetic susceptibility measurements reveal the presence of an Mn...Mn exchange interaction which is moderately antiferromagnetic ($2J = -74.0\ \mathrm{cm}^{-1}$) and is modulated by zero-field splitting effects.

The crystal structure of [Mn(TPP)]Cl in the space group I4/m has been determined [21]. The unit cell comprises two full molecules and one eighth of a molecule is unique. The Mn–N distance is 2.002(3) Å while the axial Mn–Cl distance is 2.297(15) Å. The Mn atom is displaced out-of-plane by 0.16 Å. A reverse doming of the porphyrinato core caused by crystal packing is thought to occur.

The controlled oxidation of manganous nitrate with *n*-tetrabutylammonium permanganate in the presence of benzoic acid and bpy led to the preparation of a new dinuclear complex $[\mathrm{Mn_2O(PhCOO)_2(bpy)_2(OH)(NO_3)}]\cdot\mathrm{H_2O}$ [22]. From X-ray crystallography a triply-bridged $[\mathrm{Mn_2(\mu\text{-}O)(\mu\text{-}PhCOO)_2}]^{2+}$ core with an Mn–Mn distance of 3.1405(6) Å was determined. To complete the coordination a chelating bpy and terminal OH^- (2.1582 Å) and $\mathrm{NO_3^-}$ (2.28(2) Å) are present. Magnetic studies indicate that a ferromagnetic interaction takes place between Mn(III) ions in a compressed octahedral environment. Extended Hückel calculations were employed to assess the magnetostructural relationship between ferromagnetic behavior in this complex and compression in the coordination sphere.

Proton NMR spectroscopy has been used as a structural probe in the identification of paramagnetic β-hydroxy-(methoxy)-substituted Mn(III) porphyrins [23]. The ethanolyis of (2-BzO–TPP)$\mathrm{Mn^{III}}$Cl generated the trimeric molecule [(2-O–TPP)$\mathrm{Mn^{III}}$]$_3$. Its electronic spectrum is notably different from its monomeric precursor with splitting of the Soret band absent and a broadening of all the bands. Its magnetic moment in chloroform at 293 K is equivalent to 4.6 μ_B per manganese atom. Evidence from proton NMR spectroscopy shows the presence of a head-to-tail cyclic trimeric structure with pyrrolic alkoxide groups bridging from one macrocycle to the Mn(III) ion in the adjacent macrocycle. Each Mn(III) porphyrin subunit is unique. An upfield shift of −111.5 ppm for the 3-H pyrrole at 291 K was obtained and is evidence for high-spin d^4 manganese(III)-pyrrole alkoxide coordination. In addition, the ^{1}H NMR spectrum of a series of monomeric 2-substituted Mn(III) TPP complexes have been generated and analyzed. Asymmetry imposed by substitution at the 2-position was evident in the pyrrole resonances and used as a probe in the mapping of spin densities. The electronic effect is strongly localized at the β-substituted pyrrole.

The reactivity of the dimer $\mathrm{Mn_2^{III}}$(2-OHsalpn)$_2$, 2-OHsalpn = 1,3-bis(salicylideneamino)-2-propanol, with *tert*-butyl hydroperoxide was studied in organic media [24]. The reaction which is a one-electron one, proceeds with the initial formation of a *tert*-butoxy radical and the oxidized $\mathrm{Mn^{III}Mn^{IV}}$(2-OHsalpn)$_2$OH species whose structure (**5**), shows a hydroxide ligand occupying the labile site. Addition of excess peroxide results in the evolution of singlet dioxygen and this evolution is strongly attenuated in the presence of a radical scavenger. The system was observed to oxygenate cyclohexane yielding 2-cyclohexene-1-one, 2-cyclohexen-1-ol and traces of cyclohexene oxide. Cumene was oxygenated to 2-phenyl-2-propanol and acetophenone while cyclohexane is oxygenated to cyclohexanone and cyclohexanol. From oxygen labelling experiments the oxygen in the products originates from aerobic dioxygen and not from the hydroperoxide oxidant. Thus oxygenation occurs by radical-initiated aerobic autoxidation and not via oxo-transfer from a high-valent manganese oxo species. The complex was characterized by UV–vis, IR, NMR, EXAFS, XANES and EPR spectroscopies. The kinetics of its formation were studied and found to be first-order in peroxide. This work illustrates oxy radicals formed as a result of *homolytic* one-electron cleavage of peroxide by an Mn(III) complex may yield small amounts of olefin oxidation species which is usually considered evidence for high-valent manganese oxo-transfer chemistry. This fact points to the necessity for oxygen labeling experiments in any studies which propose manganese oxo-transfer in the mechanism.



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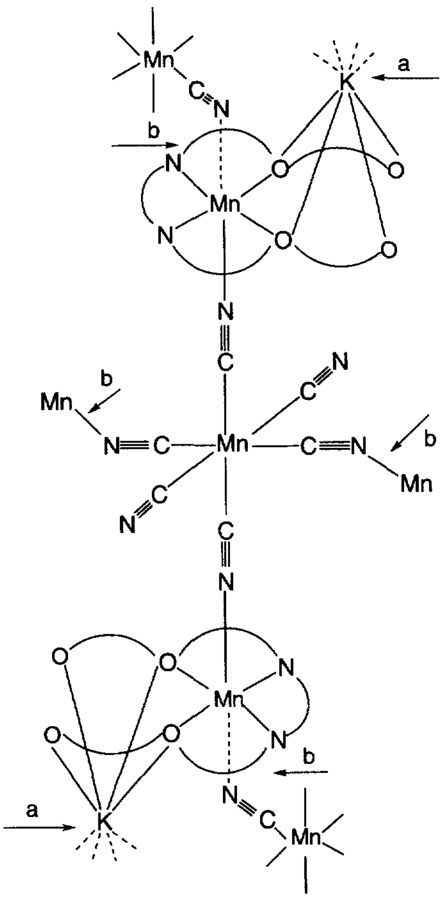
The analysis of the DNA binding/cleaving efficiency of 26 derivatives of $[\mathrm{SalenMn^{III}}]^+$ has been carried out [25]. The addition of substituents to the parent complex was found to have large effects on DNA binding cleaving efficiency and bring about changes in cleavage patterns within adenine:thymine rich target sites. The data provides evidence that both steric and electronic effects alter the DNA binding/cleaving specificity exhibited by the derivatives. In addition, it demonstrates that chiral derivatives of the parent compound exhibit enantiospecific recognition and indicate orientations relative to DNA from which the parent complex and its derivatives produce DNA cleavage.

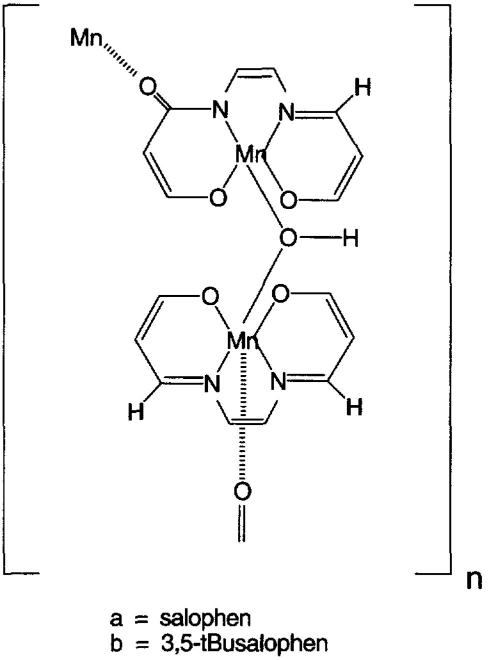
The assembling modes of manganese Schiff base complexes have been explored [26]. Two extended structures $[\mathrm{K\{Mn(3\text{-}MeOsalen)\}_2\{Fe(CN)_6\}}]_n$ and $[\mathrm{K\{Mn(3\text{-}MeOsalen)\}_2\{Mn(CN)_6\}}]_n$ (**6**), (3-MeOsalen = *N*,*N*′-ethylenebis-(3-methoxysalicylideneaminato)) were obtained. The former has a two-dimensional network derived from the cyclic octameric $[\mathrm{Mn\text{–}NC\text{–}Fe\text{–}CN}]_4$ repeating unit. It displays metamagnetic behavior derived from an interlayer ferromagnetic interaction and an interlayer weak antiferromagnetic interaction. Isostructural substitution of Fe by Mn gave the latter complex which exhibits an analogous metamagnetic behavior with a Neel transition temperature $T_N = 16$ K. Below 13.5 K at low fields this complex shows an anomalous negative magnetization.

The reaction of the Schiff bases salophen and 3,5-^{t}Bu salophen complexes (**7**), with dioxygen under controlled conditions has been explored [27]. Complexes a and



(6)

b have been structurally characterized. Complex b is a rare Mn^{III} dimer bridged by a single hydroxy group which asymmetrically bridges the two Mn atoms [unit A: Mn–O 2.009(8) Å; unit B: Mn–O 2.082(8) Å; the Mn–O(salophen) distances are much longer than those of the corresponding oxo-bridged analogues (1.78–1.84 Å)]. This complex exhibits a coupling constant of $-24.0\,\mathrm{cm}^{-1}$ which is indicative of considerable antiferromagnetic coupling between the two Mn atoms. Replacement of the hydrogen atom at the imino functionality with a methyl group led to a very different pathway depending on the solvent used. The reaction of $[Mn(Me\text{–}salophen)(THF)_2]$ with oxygen in THF was different to that with $[Mn(salophen)(THF)_2]$ and $[Mn(3,5^{t}butylsalophen)(THF)_2]$. The O_2:Mn ratio changes from 0.5:1 for $[Mn(salophen)(THF)_2]$ and $[Mn(3,5^{t}butylsalophen)(THF)_2]$ to 1:1 for $[Mn(Me\text{–}salophen)(THF)_2]$. In the case of the latter the formation of a superoxo species is proposed. The reaction products were found to be dependent on the solvent used.



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Extended structures derived from the reaction between the cationic complexes $[Mn(BS)(H_2O)]^+$ and $[Mn_2(BS)_2(H_2O)_2]^{2+}$, BS = *N*,*N*′-ethylenebis(3-methoxysalicylideneiminato) dianion, *N*,*N*′-ethylenebis(5-chlorosalicylideneiminato) dianion, *N*,*N*′-ethylenebis(5-bromosalicylideneiminato) dianion, *N*,*N*′-1,1,2,2-tetramethylethylenebis(salicylideneiminato) dianion, *N*,*N*′-*trans*-1,2-cyclohexanediethylenebis(salicylideneiminato) dianion and the anion $[Fe(CN)_6]^{3-}$ have been obtained [28]. An Mn–Fe interaction was achieved through the formation of Fe–C–N–Fe bridges. Trimeric anions $[\{Mn(BS)\}_2\{Fe(CN)_6\}]^-$ or the pentameric cation $[\{Mn(BS)\}_4\{Fe(CN)_6\}]^+$ were obtained depending on the nature of the Schiff base. X-ray analysis of the *N*,*N*′-ethylenebis(5-chlorosalicylideneiminato) trimeric anion derivative revealed a two-dimensional network layer structure [29]. Metamagnetic behavior was observed with ferromagnetism operative within a layer while antiferromagnetism operates between layers. Temperature-dependent magnetic susceptibilities are consistent with the trinuclear Mn(III)–Fe(III)–Mn(III) structure. The pentameric *N*,*N*′-(*trans*-1,2-cyclohexanediethylene)bis(salicylideneiminato) derivative comprises a two-dimensional layer containing a cyclic dodecamer as the repeating unit. Two ferromagnetic intralayer interactions were observed for this cation, namely, an interaction between Fe(III) and Mn(III) ions bridged by CN groups and an interaction between two Mn(III) ions [30].

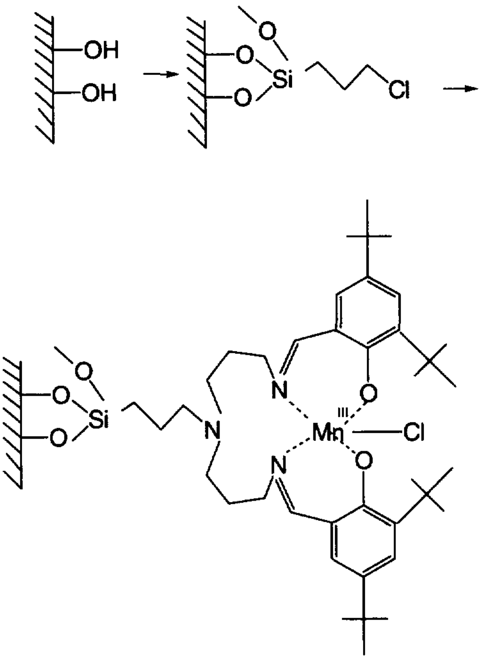
The solvent dependency on the ESR spectra of dinuclear Mn(III/IV) compounds with di-μ-oxo bridges has been studied [31]. The dinuclear compounds contained ligands tris(2-pyridylmethyl)amine, 1,4,8,11-tetraazacyclotetradecane, *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethylenediamine and *N,N'*-bis(2-pyridylmethyl)glycine were found to exhibit solvent-dependent solution ESR spectra at room temperature in acetonitrile, DMF, *N,N*-dimethylacetamide, DMSO and methanol. Studies on the temperature dependency of the ESR spectra (77–295 K) revealed that the six-line ESR signal observed can be ascribed to a spin-trapped dimeric species with a di-μ-oxo bridge rather than a monomeric species.

The kinetics of the reaction of the heterovalent oxo-bridged dinuclear Mn(III,IV) complex $[Mn_2O_2(phen)_4]^{3+}$ with NO_2^- has been explored [32]. In phen–Hphen$^+$ buffer (pH = 4–5) the complex $[Mn_2O_2(phen)_4]^{3+}$ is formed. An equilibrium constant of $K_{1H} = 35 \pm 10$ dm^3 mol^{-1} was obtained. The addition of nitrite ion resulted in the formation of adducts with the phen (1N) and aquated phen (2N) complexes respectively, and their respective association constants were determined to be $K_{1N} = 14.1 \pm 2$ dm^3 mol^{-1} and $K_{2N} = 50 \pm 10$ dm^3 mol^{-1} which are indicative of outer-sphere complexes. The latter adduct was reduced via one-electron steps to Mn(II) with a rate constant $k_{2N} = (3.33 \pm 0.6) \times 10^{-2}$ s^{-1} at 30 °C and $I = 0.10$ mol dm^{-3} for the first step. No kinetic activity for 1N was detectable under the prevailing experimental conditions.

The grafting of an Mn(III) Schiff base complex onto the internal surface of a mesoporous MCM-41 type silica through Si–O–Si bonds has been reported [33]. The synthesis delineated in (**8**) consists of an initial step in which the activated silica is treated with refluxing anhydrous toluene solution of 3-chloropropyltriethoxysilane followed by washing with diethyl ether–methylene chloride in a Soxhlet apparatus to give covalently anchored 3-chloropropylsilane moieties. The latter was treated with a toluene solution of an excess of the ligand 3-[*N,N'*-bis-3-(3,5-di-*tert*-butylsalicylidenamino)propyl]amine, (*t*-salpr), yielding the anchored moiety which was characterized by IR and ^{13}C NMR spectroscopies. Metal atoms were introduced by reacting the surface *t*-salpr ligands with $Mn(acac)_2$ in MeOH at 355 K under argon. The grafted Mn^{II} complexes suspended in saturated brine were air oxidized to give ClMn^{III}(*t*-salpr) bound to the 3-chloropropylsilane moiety. The regular porous structure of this support is maintained all throughout the covalent linking process.

The anhydrous form of the tetramanganese cluster $[Mn_4(\mu_3\text{-}O)_2(\mu\text{-}O_2CMe)_7(bpy)_2]ClO_4$ has been isolated using different starting materials [34]. This cluster had previously been obtained in its trihydrate form. It was isolated from the reaction of $[Mn_3(\mu_3\text{-}O)(\mu\text{-}O_2CMe)(OH_2)_3]MeCO_2$ with bpy and crystallizes in the monoclinic space group C2/c in a higher symmetry in comparison to the hydrated form. The Mn–O distances are in the range 1.893(7) to 2.172(8) Å while the Mn–N distances are 2.070(8) and 2.081(10) Å. The Mn–Mn distances are 2.84, 3.303(3) and 3.379(2) Å.

A new manganese complex with N_2O_3Cl coordination environment has been synthesized [35]. The complex [Mn(sal)(bpy)(MeOH)Cl]·MeOH was characterized by X-ray crystallography. The bpy and sal ligands are coordinated in the equatorial plane while the chloro and methanol ligands are in an axial position. The Mn–O distances are 1.837(3) and 1.868(4) Å while the Mn–N distances are 2.045(5) and 2.047(4) Å. The Mn–O(MeOH) distance is 2.315(4) Å while the Mn–Cl is



(8)

2.495(2) Å. Magnetic, electrochemical and spectroscopic data for this complex are presented and discussed.

A study of manganese complexes of the Schiff base ligand *N*,*N*′-ethylenebis(3-imino-1-phenyl-1-butanato), bzacen^{2-}, has been carried out [36]. The structure of [MnCl(bzacen)] has been obtained in which Mn is in a distorted square-pyramidal environment with an N_2O_2 basal plane originating from the Schiff base ligand. The Mn–O distances are 1.888(3) and 1.890(3) Å, the Mn–N distances are 1.947(4) and 1.961(4) Å, while the Mn–Cl distance is 2.415(2) Å.

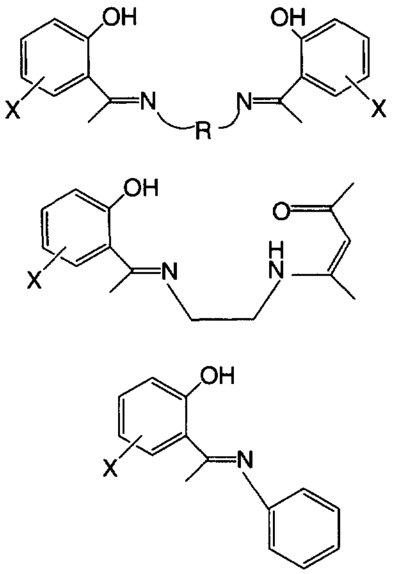
The crystal structure of (ethanol)(2,3,7,8,12,12,17,18-octaethylporphinato)-manganese(III) perchlorate has been reported [37]. It was obtained during the attempted preparation of $[Mn(OEP)]_2O$ from chloroform and hexanes. The ethanol ligand is believed to be derived from a stabilizer in the chloroform solvent used. The average Mn–N(pyrrole) bond length of 1.997(5) Å and the Mn displacement of 0.17 Å are typical for five-coordinate Mn porphyrinates possessing axial oxygen atom donor ligands. The axial Mn–O distance is 2.145(2) Å. This complex forms π–π dimers in the solid state. The mean planes of the two porphyrinato cores with close "face-to-face" contact have an interplanar distance of 3.53 Å and a lateral shift of 3.40 Å consistent with the four up/four down peripheral ethyl-group orientation. The ethanol ligand and the perchlorate anion were found to be disordered.

The solvolytic reaction of several metal salts including Mn(III) acetate in chlorosulfuric acid generated $Mn(SO_3Cl)_3$ in which the acid acts as both the medium of the reaction in addition to being a chlorosulfonating agent [38]. Furthermore, the coordinating ability of the SO_3Cl group has been further investigated by synthesizing complexes of metal tris(chlorosulfates) with strong donor organic bases of the type $[M(SO_3Cl)_3L_3]$ L = methylcyanide, py or acridine; $[M(SO_3Cl)_3L_2]$, L_2 = bpy; and $[M(SO_3Cl)_3L$, L = triphenylphosphine. Data from IR spectroscopy and magnetic susceptibility measurements are indicative of the presence of a strong interaction between the anion and the complex cations. The metal atom is hexa-coordinate in all complexes.

An assessment of structural trends in the observed diversity in Mn(III) complexes of tetradentate Schiff bases has been made [39]. A series of Mn(II) complexes of aryl substituted N_2O_2 donor set Schiff base ligands was prepared by aerial oxidation of Mn(II) precursors. The resultant complexes of stoichiometry $[MnL]ClO_4O \cdot nH_2O$ where $n = 1$–3 have been characterized by elemental analysis, IR spectroscopy, FAB MS, magnetic susceptibility measurements and paramagnetic ^1H NMR. The crystal structure of the complex $[MnL(H_2O)_2]ClO_4 \cdot H_2O$, L = Schiff base ligand, (**9**), has been obtained and it was found to comprise of a polymeric array of roughly octahedral $[MnL(H_2O)_2]^+$ cations linked via an intricate network of hydrogen bonds between the perchlorate counterion and the lattice water molecule. Further stabilization of the hydrogen bonding is achieved by π–π stabilization between the aryl ligands of the Schiff base ligand. The Mn–O(phenol) distances are 1.88(1) and 1.92(1) Å and Mn–N(imine) distances are 2.01(1) and 2.03(2) Å. The Mn...Mn separation is 5.162(4) Å. The authors surmise that the structure of a ligand with identical donor atoms can have a profound and often intriguing effect on the solid state chemistry of complexes.

Mononuclear and dinuclear Mn(III) complexes containing the *N,N′*-ethylenebis(1-phenyl-3-imino-1-butanonato), bzacen, ligand have been synthesized recently [40]. They were characterized by IR, Raman and UV–vis spectroscopies, cyclic voltammetry and X-ray diffraction. Both complexes exhibit Mn atoms in distorted octahedral environments. The mononuclear complex comprises a well separated $[Mn(bzacen)(MeOH)_2]^+$ cation and a perchlorate anion with the basal plane being occupied by two nitrogen and two oxygen atoms of the bzacen ligand while the equatorial positions are occupied by methanolic oxygen atoms. The dinuclear complex is composed of a dinuclear $[Mn_2(t\text{bzacen})_2(MeOH)_2]^+$ cation, two uncoordinated perchlorate anions and two lattice water molecules. In this complex the Mn atoms are bridged by two ketonic oxygen atoms of the bzacen ligands in which the Mn...Mn separation is 3.355(4) Å and represents the first such example of a structure exhibiting bridging ketonic oxygen atoms in Mn Schiff base complexes. The Mn–O(axial) distances of 2.294(5) and 2.296(5) Å are longer than the in-plane Mn–O distances of 1.86 and 1.91 Å. The Mn_2O_2 core in this complex forms a parallelogram rather than a rhombus as observed in other complexes containing this core type.

An attempt to synthesize linear and polar coordination polymers from the complex [Mn(L)(NCO)], L = π-electron donor salen analogues such as L^1 = *N,N′*-ethylenebis(3-hydroxy-4-naphthylideneiminate) and L^2 = *N,N′*-(1,1,2,2-tetramethylethylene)bis(3-hydroxy-4-naphthylideneiminate) and π-electron acceptor moieties



R = $(CH_2)_2$, $(CH_2)_3$, $(CH_2CH_3CH_2)$, *ortho*-C_6H_4
R' = H, CH_3
X = H, 3EtO, 5Cl, 5Br, 5F, $5NO_2$

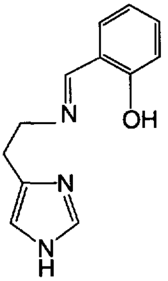
(9)

such as TCNQ, TCNE, TCBQ and TNB, has been made [41]. Only in the case of TCNE in a mixed solution of dichloromethane and acetonitrile gave tricyanoethenolate, TCEA, adducts, $[Mn(L^1)(TCEA)(H_2O)]$ and $[Mn(L^2)(TCEA)]$. Both complexes have been crystallographically characterized and results from this and magnetic susceptibility experiments show distinctive properties due to the versatility of the Mn atoms and Schiff base ligands. In the former complex manganese is in an elongated square bipyramidal environment with equatorial N_2O_2 coordination with average Mn–O distances of 1.871(3) Å and Mn–N distances of 1.957(3) Å, respectively. The two apices are occupied by a water molecule, Mn–O = 2.305(4) Å, and the nitrogen atom from a TCEA anion, Mn–N = 2.390(4) Å. In the latter complex, a dinuclear out-of-plane structure is evident with an Mn...Mn separation of 3.475(2) Å and distorted square bipyramidal geometry about each Mn atom. The equatorial plane is occupied by the same donor set as the previous complex with average Mn–O distances of 1.887(3) Å and average Mn–N distances of 1.965(3) Å. The apical sites are occupied by a phenoxy oxygen, Mn–O = 2.627(3) Å, and an oxygen atom from TCEA, Mn–O = 2.163(3) Å. Magnetic susceptibility measurements in the range 4.4–300 K indicated the presence of a weak intermolecular antiferromagnetic interaction and/or zero-field splitting operative in $[Mn(L^1)(TCEA)(H_2O)]$ while an intradimer interaction is thought to be operative for $[Mn(L^2)(TCEA)]$.

Using Ce^{4+} oxidation of Mn^{2+} in acetic acid in the presence of 2,2′-bipyridine generated an unsymmetrical complex $[Mn_2O(OAc)_2(H_2O)(NO_3)(bpy)_2](ClO_4) \cdot CH_3COOH$ [42]. It has been characterized by X-ray crystallography and reveals bridging by two acetate ligands and an oxide ion. The Mn–Mn distances are 3.137 Å and each metal atom displays Jahn–Teller distortion resulting in two distinct types of $Mn{-}O_{OAc}$ bonds with lengths of 2.180 and 1.938 Å. The $Mn{-}O_{oxide}$ distances are 1.782(5) and 1.790(4) Å and Mn–N distances are in the range 2.057(5)–2.076(6) Å. The complex is soluble in polar solvents and decomposes over a period of time leading to brown precipitates. Freshly prepared solutions in acetonitrile and water reveal no bands in electronic spectra while in acetate buffer a band at 610 nm was observed which is slowly replaced in the presence of excess ligand by bands due to the species $[Mn_2O_2(bpy)_4]^{3+}$.

Dinuclear Mn(III) and Mn(II) complexes with oxo and benzoate derivatives as bridging ligands have been prepared [43]. In particular, $[\{Mn(bpy)(H_2O)\}(\mu\text{-}O)(\mu\text{-}RCOO)_2]X_2$, where R = 2-, 3- or 4-chlorobenzoate and $X = NO_3^-$ or ClO_4^- have been obtained and their reaction with hydrogen peroxide has led to three additional complexes formulated as $[\{Mn(bpy)_2\}_2(\mu\text{-}RCOO)_2](ClO_4)_2$. The complexes were characterized by EPR, magnetic susceptibility measurements and electrochemical studies.

Manganese(III) complexes with organic ligands containing imidazole nitrogen have been synthesized [44]. In particular complexes of 2-{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}phenol (**10**) and 2-{*N*-[2-(2-pyridyl)ethyl]iminomethyl}phenol (**11**) were synthesized and characterized by IR and electronic spectroscopy, cyclic voltammetry and X-ray crystallography. Both adopt octahedral geometries.



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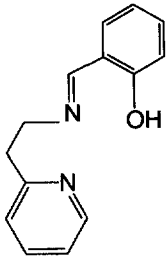

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5.3. Complexes with nitrogen donor ligands

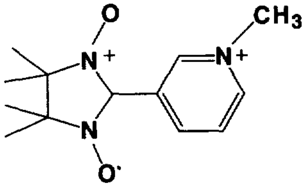
The second example of a molecular-based magnetic material containing *trans*-μ_2-*N*- σ-bonded $[TCNE]^{\cdot-}$ subunits has been obtained [45]. The structure and magnetic properties of (*meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinato)manganese(III) tetracyanoethenide, $[Mn^{III}TP'P]^+[TCNE]^{\cdot-} \cdot 2PhMe$, were obtained. This complex was prepared from the reaction of $[Mn^{III}TP'P]OAc$ with the strong acid H_2TCNE in the presence of TCNE to form acetic acid and the product. This complex is a coordination polymer in which the Mn(III) sites are bridged by *trans*- μ_2-*N*- σ-bonded $[TCNE]^{\cdot -}$ in which there are relatively short intrachain (8.587 Å) and long (≥14.756 Å) interchain Mn...Mn separations. Magnetic studies show Curie–Weiss behavior above 210 K with an effective Q value of 90.0 K which is the largest yet reported for a molecule. A 15 K T_C was obtained which is unexpectedly high and suggests that other linear chain systems may be expected to exhibit magnetic ordering at higher temperatures.

Synthetic procedures and the electrochemical characterization of four new highly chlorinated porphyrins 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin (H_2tdcdmpp), [Co^{II}(tdcdmpp)] and [M(tdcdmpp)Cl], M = Fe^{III} or Mn^{III} have been reported [46]. The same derivatives of [5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin], tdmpp, were also synthesized. The oxidation potentials of each of the eight compounds were measured in pyridine and benzonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate. The half-wave potentials of the tdcmpp complexes were shifted towards positive values while those for oxidation or reduction of the tdmpp species are shifted negatively when compared to values of oxidation or reduction of tpp complexes containing the equivalent metal ions. The anodic shifts range between 590 and 680 mV depending on the redox reaction and the solvent. These complexes were further characterized by UV–vis spectroscopy.

6. Manganese(II)

6.1. Complexes with halide ligands

The structural and magnetic properties of four salts of Mn(II) and Co(II) have been described. In particular the organic radical cations 4,4,5,5-tetramethyl-2-(1-methyl-3 or 4-pyridino)-3-oxide-4,5-dihydrido-[H]-1-imidazolyloxyl, *m*- or *p*-*N*-methylpyridinium nitronyl nitroxide, *m*-$PYNN^+$ (**12**) or *p*-$PYNN^+$ (**13**) were found to crystallize with magnetic counter anions MCl_4^{2-}, M = Mn(II) or Co(II). Their crystal structures were governed by the radical cations. For the *meta* case, the MCl_4^{2-} is located just on the pyridinium ring of *m*-$MPYNN^+$ in crystals of the salts while MCl_4^{2-} makes contact with the NO groups of *p*-$MPYNN^+$ in the *para* case. The two *meta* salts exhibit ferromagnetic behavior attributable to the *m*-$MPYNN^+$ dimer formed by the intermolecular distance between the NO group and the α-carbon. The (*p*-$MPYNN^+)_2MCl_4^{2-}$ salt exhibits antiferromagnetic behavior while the cobalt derivative exhibits ferromagnetic behavior. These differences in magnetic behavior may be rationalized in terms of a charge-transfer interaction between the metal halide and the *p*-$MPYNN^+$ moiety which differs between Mn^{2+} and Co^{2+}.



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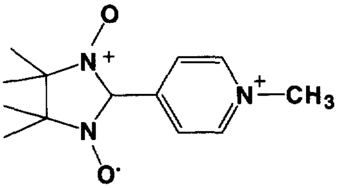

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6.2. Complexes with hydride ligands

The first salt-like manganese hydride has been synthesized recently. The reaction of potassium hydride with manganese powder under a hydrogen pressure above 3000 bar at 875 K generated the hydride. The deuteride was also obtained from potassium deuteride. X-ray diffraction of the hydride, and elastic neutron diffraction on the deuteride facilitated structure elucidation. The hydride contains isolated $[MnH_4]^{2-}$ tetrahedra and hydrogen ions exclusively coordinated by potassium cations. Magnetic susceptibility experiments show Curie–Weiss behavior with antiferromagnetic interaction below 50 K.

6.3. Complexes with oxygen donor ligands

The Mn^{2+}-catalyzed oxidation of the bisulfite ion by oxygen was determined in the pH region 4.5 at 25 °C at bisulfite concentrations in the range 1.5×10^{-1} to 1.2×10^{-2}M [47]. This reaction was found to obey a three-term rate law $-d[O_2]/dt = k_\alpha[HSO_3^-] + k_\beta[HSO_3^-][Mn^{2+}] + k_\gamma[HSO_3^-][Mn^{2+}]^2$ with $k_\alpha = 3.6\times10^{-3}M^{-1}\,s^{-1}$, $k_\beta = 1.23M^{-1}\,s^{-1}$ and $k_\gamma = 98.6M^{-1}\,s^{-1}$ at pH = 4.5, 25 °C and ionic strength 0.050M. The kinetic behavior of the reaction was found to resemble markedly that of the uncatalyzed reaction, i.e. is independent of oxygen concentration, and $S_2O_7^{2-}$ and HSO_3^- are intermediates in the reaction. This reaction is catalyzed by $S_2O_8^{2-}$ and is strongly inhibited by methanol.

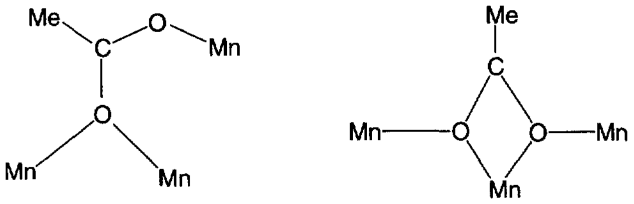
The ESR spectra of Mn^{2+}-exchanged A zeolites as a function of the monovalent co-cation, Mn^{2+} content, recording frequency and temperature have been studied [48]. The X- and Q-band ESR spectra are strongly influenced by the nature of the co-cation and the hydration state of the molecular sieve. Three new Mn^{2+} species were observed allowing a direct quantitative determination of zero-field splitting parameters in hydrated zeolites. In fully dehydrated species two species are observed.

The synthesis of a new, layered perovskite $YBaMn_2O_5$ has been described [49]. The phase is stable only when the oxygen content is close to the non-stoichiometric value where the average Mn oxidation state is +2.5, this is a very unusual oxidation state for a perovskite oxide. This leads to Mn^{II}/Mn^{III} valence ordering and insulating electronic behavior below 300 K resulting in a ferromagnetic state with a small resultant moment below the ordering transition at 167 K.

The use of hydrothermal synthesis in the engineering of coordination architecture has been demonstrated recently [50]. By reacting manganese dichloride with an excess of benzene-1,3,5-tricarboxylic acid (trimesic acid) and KOH in aqueous solution at 220 °C for three days followed by cooling to room temperature the complex $[Mn_3\{C_6H_3(CO_2)_3\text{-}1,3,5\}_2]$ was obtained. The structure of this complex comprises Mn(II) ions and the trianion of trimesic acid in a 3:2 ratio giving a neutral structure with an underlying threefold symmetry in which the carboxylates reveal both bridging and terminal coordination. The basic structural feature is a linear Mn_3 unit lying along the *c*-axis in which all the metal atoms have approximately octahedral geometry. The central manganese atom is bridged to two outer metal atoms via oxygens from six different trimesic acid trianions, the Mn...Mn distance is 3.01 Å. Both oxygen atoms in the carboxylate functionality have different functions within the lattice, one bridges two metal atoms within a trimer (Mn–O = 2.27, 2.16 Å) while the other coordinates in a terminal (Mn–O = 2.08 Å) fashion to an Mn atom of the adjacent trimer. Each trimer has six nearest neighbors, three below and three above with the shortest inter-trimer distance between Mn atoms of 5.01 Å. On looking down the *c*-axis the structure appears as alternating trimers and pairs of ligand trianions. The ligands are parallel yet staggered such that the carboxylated substituted carbon atoms of one ring lie directly above the unsubstituted ring carbon atoms of another ring with a ring separation of 3.39 Å. The Mn...Mn distance of 3.0 Å is significantly smaller than observed in other complexes with carboxylate bridges and may be due to efficient parallel stacking of the ligands. Magnetic susceptibility measurements have been carried out, two pathways for antiferromagnetic coupling have been observed.

A comparative study of the binding of Mn^{2+}, Ca^{2+} and Mg^{2+} to *E. coli* ribonuclease H and exonuclease III enzymes has been carried out [51]. The results from these experiments characterize the thermodynamics of metal ion binding and selectivity. The binding parameters for Ca^{2+} and Mg^{2+} are similar with a positive entropy term indicating release of a water molecule. One binding site was available for both of these ions. In contrast, the binding profile for Mn^{2+} provided evidence for at least two types of sites with one exhibiting exothermic binding while the other exhibited endothermic binding. These results have implications in the interpretation of previous crystallographic and mechanistic studies of magnesium-dependent nucleases where Mn^{2+} was often substituted for Mg^{2+} and are relevant to the issue of one-metal vs two-metal-ion mechanisms for nucleic acid hydrolysis.

Crystalline anhydrous bis(acetato)manganese(II) has been isolated from superheated acetonitrile under autogeneous pressure recently [52]. Single crystals of the β-$Mn(O_2CMe)_2$ were obtained as a byproduct from the reaction of $[Mn_3O(O_2CMe)_6(py)_3]$ and terephthalic acid in acetonitrile at 150 °C under autogeneous pressure. The large colorless crystals of the title compound were separated from a dark green amorphous phase. In an effort to enhance yields dehydration of $Mn(O_2CMe)_2 \cdot 4H_2O$ at 110 °C under dynamic vacuum for 12 h gave a second phase α-$Mn(O_2CMe)_2$ which can be readily distinguished by X-ray powder diffraction. The IR spectra and elemental analyses of these two phases are indistinguishable. The structure comprises a complex three-dimensional network which is constructed from a trimer of acetate-bridged Mn(II) centers. A seven-coordinate Mn polyhedron shares one face with a distorted octahedron about a second Mn polyhedron and an edge with the distorted polyhedron around a third polyhedron. Since there are only two acetate ligands for each Mn atom extensive ligand bridging is a necessity to fill the coordination spheres of the manganese atoms. Two coordination geometries are apparent (**14**). The oxygen atoms from the five type I acetate ligands which bridge two Mn atoms form the principal backbone of the trimer. The triply-bridged Mn...Mn distance is 3.202(1) Å while the doubly-bridged Mn...Mn distance is 3.373(1) Å. The type I acetate oxygens join three trimers and with the terminal oxygen atoms from the type I acetate ligands link the trimers into a three-dimensional network with inter-trimer contacts of 3.816(1) and 3.887(1) Å. Interestingly, the shortest Mn–O distances are to the non-bridged oxygen from the type I acetate ligands, average 2.14 Å. The strongest influence on the Mn–O distances appears to be the seven vs six-coordination of the Mn atom, i.e. when Mn is seven coordinate the Mn–O length is 2.28 Å (av.) whereas for Mn = 6 coordination, the average Mn–O distances are 2.17 Å.



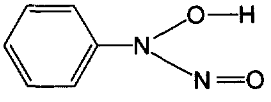
(**14**)

A new two-dimensional potassium manganese(II) hydroxyvanadate $K_2Mn_3(OH)_2(VO_4)_2$ has been isolated [53]. It has a layered structure, the $[Mn_3(OH)_2(VO_4)_2]_n^{2n-}$ layers have planes of $MnO_4(OH)_2$ octahedra with 1/4 Mn vacancies to which VO_4 tetrahedra are linked on both sides via three vertices with the fourth vertex pointing into the interlayer space where the K^+ ions are situated.

The reaction of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ with benzene-1,2-dioxyacetic acid ($bdoaH_2$) in a 4:1 ethanol–water mixture generated the pseudo-seven-coordinate complex $[Mn(bdoa)(H_2O)_3]$ in high yield [54]. An X-ray crystallographic study has been carried out and shows the quadridentate bdoa ligand forming a planar girdle about the metal atom with the carboxylate oxygen atoms being *trans* to one another while the internal ether linkages are weakly chelated. The other three positions are occupied by three water molecules which lie in a meridional plane. The average Mn–O(carboxylate) distance is 2.199 Å while the average Mn–O(ether) distance is 2.413 Å and average Mn–O(H_2O) distances are 2.146 Å. Magnetic, conductivity and voltammetric studies have been carried out. The ability of this complex to catalyze the disproportionation of hydrogen peroxide has been verified.

The novel monomeric complex $Na_2[Mn(Me_3NCH_2CH_2CO_2)_4(H_2O)_2](ClO_4)_4 \cdot 4H_2O$ has been prepared and characterized [55]. The Mn atom is octahedrally coordinated in a distorted fashion by a pair of *syn* monodentate carboxylato ligands, a pair of *anti* monodentate carboxylato ligands and two aqua ligands. The Mn–O distances are in the range 2.167(3)–2.204(3) Å.

The crystal structure of an Mn complex of cupferron (**15**) has been elucidated in order to gain structure sensitive information regarding the binding scheme of the nitroso group [56]. In this complex the Mn is in a distorted octahedral environment defined by four oxygen atoms from two cupferron ligands and two oxygen atoms of the nitroso groups of two adjacent cupferron ligands with Mn–O distances in the range 2.142(2)–2.198(2) Å. In addition, each nitroso oxygen atom coordinates to two Mn ions thereby resulting in an $(\text{–Mn–O–Mn})_n$ network which stabilizes the crystal structure.



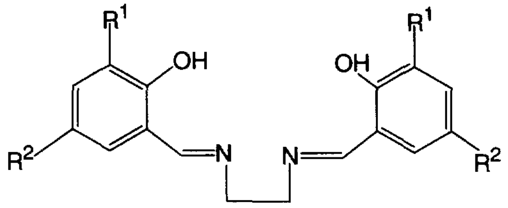
(15)

The oxidation of the heteropolyanion $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ with potassium persulfate has been investigated [57]. Mixed-valence products were isolated, namely, a green potassium salt of $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{9-}$ and a brown potassium caesium salt of $[Mn_4(OH)_2(PW_9O_{34})_2]^{9-}$. X-ray crystallography reveals that these complexes are one and three-electron oxidized derivatives respectively of the starting complex. Analysis of the Mn–O bond distances in these complexes shows slight variations which suggest that oxidation has occurred at the aquated Mn centers of the parent complex. Magnetic measurements on $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{9-}$ reveal Curie–Weiss law behavior.

6.4. *Complexes with oxygen and nitrogen donor ligands*

The first Mn L-edge spectrum of manganese catalase has been obtained [58]. Reduced and superoxidized Mn catalase was examined by fluorescence-detected X-ray absorption spectroscopy. The spectrum of reduced Mn(II)Mn(II) catalase was simulated with a ligand field of 0.80 eV. Experimental mixed-valence simulations of the L-edge spectrum of Mn_{16} generated a ratio of 8.5 Mn(II) to 7.5 Mn(III). This simulation when applied to the superoxidized catalase predicted an Mn(III) to Mn(IV) ratio of 0.7:1.3. Correction for 8% photoreduction gave the more correct ratio of 1:1.

The preparation and remarkable structural chemistry of a series of complexes prepared from substituted derivatives of H_2salen (**16**), has been reported [59]. Fine tuning of the N_2O_2 donor set Schiff base ligand can be achieved through substitution at various positions in the phenyl rings which was found to have a profound effect on the complexes obtained. The reaction of $Mn(ClO_4)_2 \cdot 4H_2O$ with the ligand normally results in Mn(III) complexes but using electron-withdrawing substituents on the ligand, e.g. 3-Br or 5-NO_2 gives an Mn(II) complex. In the case of the 5-NO_2 salen derivative, an Mn(II) complex contaminated with a small amount of Mn(III) species was obtained indicating that this ligand is “borderline”. The use of a more rigorous oxidizing agent $[FeCp_2][FeCl_4]$ was found to drive the reaction all the way to the Mn(III) species [Mn(nsalen)Cl(H_2O)]. These complexes have been characterized by FAB MS, electrochemistry and X-ray crystallography (six complexes) which reveal the retention of an octahedral manganese environment but with great diversity in their supramolecular structures. In the case of the 3,5-dichloro and 5-bromo salen derivatives the octahedral coordination is completed by capping *trans* water molecules. Pairs of these molecules associate via a combination of π-aryl stacking interactions and hydrogen bonds between the water molecules and phenolic oxygen atoms generating dimers resembling the bis-μ-aqua-bridged dimers.

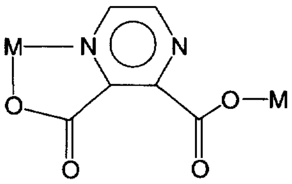


H_2salen	$R^1 = R^2 = H$
H_2eoalen	R^1 = EtO, $R^2 = H$
H_2csalen	$R^1 = H$ $R^2 = Cl$
H_2bsalen	$R^1 = H$ $R^2 = Br$
H_2dcsalen	$R^1 = R^2 = Cl$
H_2dbsalen	$R^1 = R^2 = Br$
H_2bcsalen	R^1 = Br, $R^2 = Cl$
H_2bmosalen	R^1 = MeO, $R^2 = Br$
H_2nsalen	R^1 = H, $R^2 = NO_2$
H_2bnsalen	R^1 =Br, $R^2 = NO_2$

(16)

The spin distribution in the $S=2$ ground state of an antiferromagnetically coupled Mn(II)Cu(II) pair has been determined by polarized neutron diffraction and theoretical computations [60]. In particular, the dinuclear compound [Mn(Me_6-[14]ane-N_4)Cu(oxpn)](CF_3SO_2)$_2$, Me_6[14]ane-N_4=(±)-5,7,12,14-hexamethyl-1,4,8,11-tetrazacylotetradecane and oxpn=*N*,*N*′-bis(3-aminopropyl)oxamido, consists of bridged [Mn(Me_6-[14]ane-N_4)Cu(oxpn)]$^{2+}$ cations and non-coordinated triflate anions. The experimental spin density was deduced from polarized neutron diffraction studies recorded at 2 K and 50 kOe. Large positive densities were found on the Mn atoms while that on the Cu atoms was weak and negative. Both spin densities are delocalized from the metal centers toward the terminal and bridging atoms surrounding the metal centers. These results have been compared to theoretical data obtained from two types of computational approaches, namely: (i) the incorporation of spin delocalization into the Heitler–London scheme using magnetic orbitals in the EH formalism and (ii) two types of DFT methods. The results from computational efforts were found to compare fairly well with those from experimental data.

Manganese(II) and Cd(II) complexes of singly and doubly deprotonated forms of 2,3-pyrazine dicarboxylic acid, pyzdc, have been prepared recently [61]. The use of dilute aqueous solutions facilitated slow polymer formation and four compounds were obtained in crystalline form suitable for single crystal X-ray diffraction studies. The crystal structure of $[H_3O]_{2x}[M(pyzdc)_2]_x$ shows each metal ion to be *cis* coordinated by chelation interactions to two ligands. The remaining *cis* positions are occupied by oxygen atoms from carboxylate groups not involved in chelation on two neighboring units. This leads to extended chains of metal ions which are double bridged by $pyzdc^{2-}$ ligands which coordinate in the manner shown (**17**). Electrical neutrality is maintained by the presence of H_3O^+ ions in the lattice. The Mn–O distances are 2.1486(9) and 2.136(1) Å while the Mn–N distance is 2.308(1) Å. Thermogravimetric analysis shows this complex to be stable to 150 °C, decomposition occurs over the range 150–265 °C with the loss of two moles of H_2O and CO_2, respectively. Magnetic susceptibility studies reveal a magnetic moment of 5.90 μ_B at 82 K indicative of weak antiferromagnetic exchange. The crystal structure of the compound $[M(pyzdc)_2(H_2O)_2]_x \cdot 2xH_2O$ shows double chains of manganese ions in which the $pyzdc^{2-}$ ligands furnish O–C–O bridges between metals in each chain and by chelate interaction with metals in the other chain involving a ring nitrogen and a carboxylate oxygen of the second carboxylate group giving rise to a “ladder-like” motif. The Mn–O distances are in the range 2.115(2)–2.226(2) Å while the Mn–N distance is 2.294(2) Å. In addition two *cis* coordinated and two lattice water molecules are present. Thermogravimetric analysis reflects the presence of the latter as the compound undergoes decomposition at fairly low temperatures with the loss of three water molecules over the range 50–175 °C and a fourth water molecule between 175 to 320 °C. Cryomagnetic studies indicate that the magnetic moment decreases from 5.71 μ_B at 82 K to 2.27 μ_B at 1.9 K indicating the presence of significant antiferromagnetic exchange.



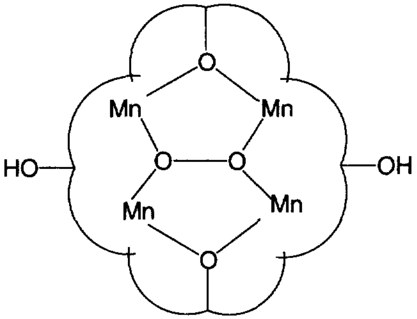
(17)

The temperature dependence of electron transfer in a mixed-valence manganese complex has been studied [62]. A zero or very small valence shift in the study of the $Mn^{II}Mn^{III}$ complex $[ttacnMn^{II}(\mu\text{-}OH)(\mu\text{-pivalonato})_2Mn^{III}ttacn](ClO_4)_2$ was discovered in spite of the fact that a diffraction study showed that at room temperature the $Mn^{II}O$ and $Mn^{III}O$ bond lengths differ by as much as 0.14 Å. Synchrotron radiation diffraction studies were carried out at 298, 62 and 20 K and showed a gradual increase in the asymmetry of the structure of the complex with lowering of temperature. One of the perchlorate anions which was disordered at room temperature became fully ordered at 20 K. This study shows that sub-liquid-nitrogen temperatures are often essential for a full characterization of mixed-valence species.

The X-ray structures, IR spectra and magnetism of two novel metallopolymers containing Mn ions involved in unprecedented arrangements with ligands derived from $[TCNQ]^{-\cdot}$ have been studied [63]. The rapid mixing of methanolic solutions of $[Mn(MeCN)_4][BF_4]_2$ and $[^nBu_4N][TCNQ]$ generated instantaneously a purple microcrystalline solid formulated as $Mn(TCNQ)_2(MeOH)_2$. Slow diffusion of the parent compounds in MeOH gave blue triclinic parallelpipeds of $[Mn(TCNQ–TCNQ)(MeOH)_2 \cdot MeOH]_\infty$ where (TCNQ–TCNQ = σ-dimerized $[TCNQ]^{-\cdot}$). From X-ray crystallography the complex comprises a 2-D network of six-coordinate Mn(II) ions equatorially bound to four outer nitrile groups of the TCNQ ligand. Since the tetradentate anion is non-planar it leads to a staircase motif in which each "step" is comprised of infinite chains of Mn(II) ions joined by metallacyclic rings involving *cis*-nitriles lying in the same plane. This two-dimensional structure is stabilized by interlayer hydrogen bonding due to axial MeOH ligands and interstitial MeOH molecules between the layers. Slow diffusion of the reactants in a MeOH/MeCN mixture gave purple monoclinic needles of $[Mn(TCNQ–TCNQ)_{0.5}(MeOH)_2]_\infty$ in which the Mn(II) ions are coordinated by tetradentate $[TCNQ–TCNQ]^{2-}$ and didentate $[TCNQ]^{-\cdot}$ ligands; the latter acting as bridging ligands through the 1,2 dicyano positions and the two unligated N–C groups pointing outwards from the edges of the zigzag layers towards axial MeOH ligands in the adjacent layers. From magnetic studies Curie–Weiss behavior for the former complex was observed between 5 and 300 K, $\mu_{eff} = 5.9$ BM; while the latter compound obeys the Curie–Weiss law over the same temperature range but exhibits a higher moment, $\mu_{eff} = 6.9$ BM, corresponding to the presence of one $[TCNQ]^{-\cdot}$ radical per Mn(II) ion.

The first manganese containing complex which carries out catalase-like reactivity while retaining a tetranuclear structure has been synthesized [64]. The reaction of $Mn^{II}(ClO_4)_2 \cdot 6H_2O$ with 2-OHpicpn and 1 equiv of NaOMe in methanol gave a tan powder which was recrystallized from acetonitrile to give orange crystals of $[Mn(2\text{-}OHpicpn)]_4(ClO_4)_4$ whose crystal structure shows it to contain Mn atoms which are spanned by alkoxide bridges. Within each Mn coordination sphere are a pyridine nitrogen, an imine nitrogen and an alkoxide oxygen each from two different ligands to give a rhombically distorted octahedron. The pyridine nitrogen–Mn bonds average 2.40 Å and are *trans* to the Mn–alkoxide bonds (2.11 Å) while the imine nitrogen atoms are *trans* to one another with intermediate bond lengths of 2.22 Å. The complex is highly efficient $V_{max} = 140\ s^{-1}$ but has a low binding constant which may be a reflection of a significant rearrangement of bonds prior to the formation of the peroxo intermediate. An intermediate (**18**), which is consistent with this chemistry has been proposed.

The preparation, crystal structure and magnetic behavior of the first two-dimensional, infinite sheet-like mixed-valence Mn(II,III) complex $[\{Na_2Mn_4(sal)_4(pyca)_4(MeOH)_2\}_n] \cdot 2nH_2O$, Hpyca = pyridine-2-carboxylic acid, has been achieved [65]. The structure comprises an $[Mn_4(sal)_4(pyca)_4(MeOH)_2]_n^{2n-}$ anion, $2nNa^+$ cations and $2n$ non-coordinated H_2O. Within each $[Mn_4(sal)_4(pyca)_4(MeOH)_2]_n^{2n-}$ unit two six-coordinate Mn(II) ions are located at



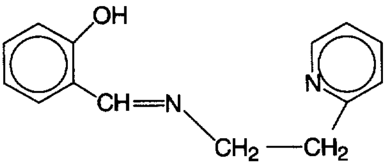
(18)

symmetry centers and two six-coordinate Mn(II) are present. In the unit, two of the Mn atoms are connected by either a salicylate or pyridine carboxylate in a *syn–anti* configuration while two other Mn atoms are bridged by two oxygen atoms of two pyridine carboxylates. The sodium cation is six-coordinate with contacts to six oxygen atoms of carboxylates groups. The magnetic behavior of this complex has been studied in the temperature range 1.4–300 K.

The first example of a bis-monohelical manganese(II) complex has been obtained [66]. The ligand 6,6''''-dimethyl-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine (dmqpy) was suspended in a methanolic solution of $MnCl_2 \cdot 4H_2O$ and refluxed yielding a clear yellow solution. Addition of $LiClO_4$ and cooling generated pale yellow microcrystals of $[Mn_2(dmqpy)(H_2O)_2(\mu\text{-}Cl)][ClO_4]_3 \cdot 4H_2O$. An X-ray crystallographic study revealed the molecule to be centrosymmetric and the dmqpy ligands were found not to adopt a double helical but rather a monohelical disposition about the Mn(II) atoms in the dimer. The coordination about the Mn atoms is distorted pentagonal-bipyramidal in which one dmqpy molecule twists to form the equatorial plane and one of the apical positions is occupied by the water molecule and the other occupied by a chlorine atom. No intermolecular stacking interactions were observed in the crystal structure but six water molecules and the perchlorate anions participate in several hydrogen bonding systems linking the molecules to form infinite chains. The Mn...Mn distance is 4.726 Å, the Mn–Cl distances are 2.208(4) and 2.587(2) Å, while the Mn–N nitrogen distances are in the range 2.297(4)–2.557(4) Å and 2.279(4)–2.432(4) Å for Mn(1) and Mn(2), respectively. The Mn–O(H_2O) distances are 2.208(4) and 2.274(3) Å for Mn(1) and Mn(2), respectively.

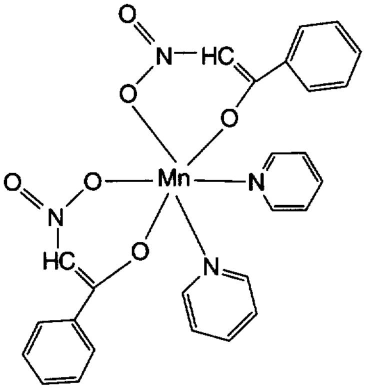
Transmetallation reactions with solutions containing Mn(II) acetate or formate have been studied recently [67]. Transmetallation of $[Ba(H_2L)(H_2O)_2](ClO_4)_2$ with manganese(II) acetate tetrahydrate in methanol gave both the pentamanganese(II) complex $[Mn_5(L)_2(CH_3COO)_2(ClO_4)_2](ClO_4)_2$ or the tetramanganese(II) complex $[Mn_2(L)(CH_3COO)]_2(ClO_4)_2$ where L is the macrocyclic ligand formed from the [2+2] condensation of 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol. Once formed these complexes were stable in solution. The specific complex formed in solution was found to be more dependent on the treatment of the methanolic Mn(II) acetate solution before addition to the barium complex rather than the conditions of the transmetallation reaction. Using Mn(II) formate during the transmetallation generated the tetranuclear complex $[Mn_2(L)(HCOO)]_2(ClO_4)_2]$. The complexes were characterized by X-ray crystallography, and electrochemical and magnetic studies. The tetranuclear complexes exhibit $Mn_4(alkoxide)_4$ cubane cores.

The novel electrochemical syntheses of a series of salicylaldiminates (**19**), R-salaepH, of Mn(II) and Mn(III) has been reported [68]. The electrochemical behavior has been studied by cyclic voltammetry. Electrochemical oxidation of anodic manganese in an acetonitrile solution of the Schiff base, R-salaepH, gave the neutral Mn(II) compounds $[Mn(R\text{-}salaepH)_2]$ or cationic compounds of Mn(III) such as $[Mn(R\text{-}salaepH)_2](ClO_4)$ where the perchlorate anion resulted from the use of tetraethylammonium perchlorate as a supporting electrolyte. The crystal structure of $[Mn(5\text{-}NO_2salaep)_2]$ has been obtained, the Mn atom is coordinated by pyridine nitrogen (Mn–N = 2.278(3) Å), a phenolate oxygen (Mn–O = 2.093(3) Å) and an imine nitrogen (Mn–N = 2.267(3) Å) atom from each ligand to give a distorted octahedral geometry.



(19)

A *cis*-dipyridine complex of bis(ω-nitroacetophenonato)manganese(II) in which the (ω-nitroacetophenonato), (ω-nap), ligands chelate the manganese center forming a six-membered ring with a bite angle of 80.13(11)° has been obtained (**20**) [69]. The metal to nitro oxygen distance (2.175 Å) versus the metal to carbonyl oxygen distance (2.118 Å) is longer indicating a stronger bond in the case of the latter and is suggestive of a keto–enol mechanism between solution and solid state which precedes the binding of the ω-nap ligand to the metal.



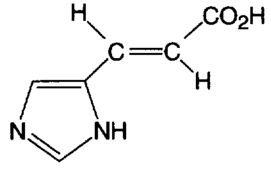
(20)

The dinuclear complex $[Mn_2(H_2O)_6(bpm)(SO_4)_2]$ has been prepared and structurally characterized [70]. The coordination geometry about the Mn atoms is octahedral with an average Mn–N distance of 2.31 Å while the Mn–O(H_2O) distance is 2.16 Å and the Mn–O(SO_4^{2-}) distance is 2.069 Å. The coordinated sulfato groups are tetrahedral but their nonbonding oxygen atoms are disordered with a 6:4 ratio. Results from IR and ESR are discussed and magnetic susceptibility data indicate a weak antiferromagnetic spin exchange with $J = -9.96\ \mathrm{cm}^{-1}$.

Studies aimed at clarifying the role of counterions in the synthesis of Mn(II) complexes has led to the synthesis and structural characterization of a new mono- and polynuclear Mn complex [71]. The mononuclear complex $[Mn(bpm)_2(H_2O)]^{2+}$ possesses a distorted octahedral coordination with an average Mn–N distance of 2.254(3) Å, the oxygen atoms of the water ligands are *cis* with respect to the bpy ligands and the average Mn–O length is 2.161(3) Å. The polynuclear complex $[Mn(bpm)(NO_3)_2]$ exhibits a seven-coordinate environment which is distorted capped octahedral. In this complex the Mn atom is bonded to four nitrogen atoms at an average distance of 2.350(4) Å and to three oxygen atoms of a mondentate nitrate ligand Mn–O = 2.197 Å and two didentate nitrate ligands at a distance of 2.388(4) and 2.311(4) Å. The remaining two nitrogen atoms of each bpm ligand are bound to other Mn(II) ions resulting in a zigzag one-dimensional polymeric chain in which the Mn...Mn separation is 6.234(2) Å thereby facilitating a weak magnetic interaction as revealed by magnetic studies where $J = 0.93\ \mathrm{cm}^{-1}$.

The synthesis of two new Mn(II) salicyclates which exhibit catalytic behavior towards hydrogen peroxide has been achieved [72]. The reaction of $[Mn_2(Hsal)_4(H_2O)_4]$ with an excess of bpy in aqueous ethanol gave yellow crystals of the complex $[Mn(Hsal)_2(bpy)]\cdot H_2O$ while the green complex of empirical formula $[Mn(Hsal)_2(phen)]$ precipitated in the analogous reaction with phen. An X-ray crystal structure of the former reveals that it is polymeric in nature with $\{Mn_{0.5}(Hsal)(bpy)_{0.5}H_2O_{0.5}\}_n$ as the asymmetric repeat unit. The Mn atom is six coordinate being bonded to the two nitrogen atoms of the bpy ligand and one carboxylate oxygen atom of each of the four salicylate ligands. The coordination of the salicylate ligands is novel when compared to previously synthesized manganese complexes. Each salicylate ligand coordinates to a pair of neighboring Mn atoms in an asymmetric *syn–anti* bridging mode thereby forming spiral chains parallel to the twofold screw axis. In the presence of added imidazole both complexes catalyzed the degradation of hydrogen peroxide with the bpy complex being more active. In a related paper [73], the synthesis of a manganese(II) complex of E-urocanic acid (**21**), has been described. It was produced from the reaction of Mn(II) chloride tetrahydrate with sodium *E*-urocanate in aqueous media. As a result of X-ray crystallographic studies two distinct isomers of the complex were seen. They differ in their disposition of the amine nitrogen of the imidazole ring with respect to the carbon–carbon double bond. In one isomer it is cisoid while in the other it is transoid. The geometry about each manganese atom is approximately octahedral and being coordinated to two imine nitrogen atoms of two urocanate anions which are *trans* to each other and four water molecules. The Mn–N lengths are 2.190(2) and 2.249(2) Å while the Mn–O distances range from 2.202(2) to 2.249(2) Å.

Further characterization by means of EPR and CV was carried out. In the presence of imidazole this complex catalyzed the disproportionation of hydrogen peroxide.



(21)

A manganese(II) complex of quinaldinic acid has been synthesized and structurally characterized [74]. The complex $[Mn(C_{10}H_6NO_2)_2(H_2O)_2]\cdot{}_2C_2H_5OH\cdot 2H_2O$ comprises a six-coordinate Mn atom with two didentate quinaldinate ligands and two water molecules in *trans* configurations. The crystal is stabilized by an extended hydrogen-bonding network incorporating two additional water and ethanol molecules. The Mn–O(carboxylato) distance is 2.125(2) Å, the Mn–N length is 2.324(3) Å and the Mn–$O(H_2O)$ length is 2.209(3) Å.

Complex formation between the Mn(II) ion and pyrazinic acid in the presence of the cyanate anion has been investigated [75]. This has led to the synthesis and characterization of the complex $[NaMn(pyz)(NCO)_2(H_2O)_2]$ which is insoluble in many polar solvents as well as non-polar ones. Characterization by IR and Raman spectroscopies suggested the presence of a didentate N,O pyrazinato anion, aqua ligands and Mn–O ligated cyanato groups. An X-ray crystallographic study indicates that the pyrazinato ligand chelates the Mn atom via its ring nitrogen (Mn–N = 2.320(4) Å) and a carboxylate oxygen (Mn–O = 2.284(3) Å) in a five-membered chelate. The metal atom is further coordinated by three oxygen atoms from three μ(O,O,N)-bridging cyanato ligands in a *fac* arrangement with Mn–O distances in the range 2.144(4)–2.307(4) Å and a bridging aqua molecule at an Mn–O distance of 2.284(3) Å. The sodium atom is bonded to three bridging cyanato ligands in a *fac* arrangement and three water molecules.

The structure of the polymeric (aqua-1κ*O*)bis[(*R*,*R*)-tartrato-1$\kappa^2O^1,O^2{:}2\kappa^2O^3,O^4$] dimanganese(II) trihydrate has been determined [76]. It is comprised of corrugated polymeric sheets of dimeric $[Mn_2\{(R,R)\text{-}C_4H_2O_6\}_2\cdot H_2O$ units and water molecules. The manganese ions are coordinated by two (*R*,*R*)-tartrate ligands in a *cis* arrangement. The Mn–O distances vary between 2.105(4) and 2.318(3) Å, the dimers are linked together through carboxylate oxygen atoms. The Mn...Mn distance is 5.527(2) Å.

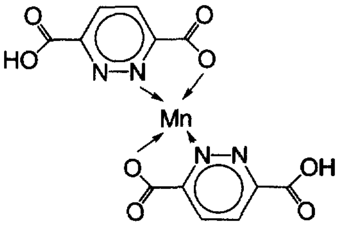
The synthesis and characterization of mono, bis and tris complexes of 2-methylpyridine-*N*-oxide (2-PyCO) with manganese halides and nitrates and their reactivity towards sulfur dioxide in the solid state and in toluene slurries at room temperature has been studied [77]. In addition, their reactivity with sulfur dioxide at high temperatures has been studied using TGA and in the solid state at high temperatures. The complexes $[Mn(2\text{-PyCO})_nX_2(H_2O)_x]$, $n = 1$–3, X = Cl, Br, I and NO_3, and $x = 0$–3 with the exception of the chloride derivative react with sulfur dioxide in the solid state and at room temperature. The nitrate derivatives fix most

SO_2 and show a displacement of the nitrate group by the sulfate. An increase in the temperature in general tends to disfavor this reaction such that the amount of sulfur dioxide fixed decreases at high temperature. Desorption studies were carried out to elucidate the binding mode of sulfur dioxide.

The synthesis and magnetism of μ-4-nitrophthalato Mn(II) dinuclear complexes, has been described [78]. They were characterized by elemental analysis, IR, molar conductance, electronic reflection spectroscopy and ESR. Based on these studies they are proposed to have extended 4-nitrophthalato-bridged structures and to consist of two Mn(II) atoms in a distorted octahedral environment. They were further characterized by variable temperature magnetic susceptibility studies.

As an extension of previously reported studies on analogous copper systems the synthesis crystal structure and magnetic properties of a chloroanilate-bridged Mn(II) chain compound, $[Mn(bpy)(CA)]_x$ where CA = the dianion of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, chloroanilate, has been reported [79]. From X-ray crystallography it can be seen that its structure formally is comprised of neutral [Mn(bpy)(CA)] units in which the chloroanilate anion serves as a bridging ligand between the metal centers thereby leading to infinite chains exhibiting a zigzag pattern along the *b*-axis with bpy ligands stacking between the chains. The Mn atom is in a distorted octahedral environment with Mn–O distances in the range 2.170(2) to 2.187(2) Å and Mn–N distances of 2.224(2) and 2.225(2) Å. The chloroanilate ring is planar and the distance between adjacent Mn atoms inside a chain is 8.142(1) Å. Variable temperature magnetic susceptibility and EPR data reveal the presence of a weak antiferromagnetic exchange interaction with $J = -0.20\ \mathrm{cm}^{-1}$.

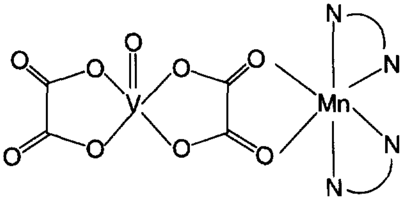
The coordination behavior of the ligand 3,6-dicarboxypyridazine, H_2DCP, with manganese has been explored [80]. Unlike in Cu(II) and Fe(II) complexes containing this ligand the reaction with Mn(II) chloride gave a mononuclear rather than dinuclear complex. The complex $[Mn(HDCP)_2(H_2O)]\cdot 2H_2O$ was characterized by X-ray crystallography and shows this ligand binds to the metal in a didentate fashion and displays a *trans* coordination mode (**22**). The Mn atom occupies a slightly deformed octahedral coordination, coordinating to two carboxylic acid-derived oxygen atoms (Mn–O = 2.150 Å) in addition to two equivalent nitrogen atoms of the pyridazine rings (Mn–N = 2.298(2) Å). The two axial positions are occupied by water molecules with the Mn–O(H_2O) distance being 2.160(2) Å.



(22)

The first oxalate-bridged dinuclear manganese vanadium complexes have been synthesized [81]. The complexes $[MnVO(ox)_2(L)_2]$, ox = oxalate dianion, L =

phen, bpy and 4,4′-dimethyl-2,2′-bipyridyl, were characterized by IR, elemental analysis, conductivity measurements and EPR and are proposed to have extended oxalato-bridged structures comprising vanadyl ions and manganese(II) ions in a distorted octahedral environment (**23**). In the case of the phen derivative, the magnetic susceptibility data were measured over the range 4.1–300 K and analysis of the data generated an exchange integral of $J = -30.9\ \mathrm{cm}^{-1}$ which indicates an antiferromagnetic exchange interaction between the metal ions.



(23)

6.5. *Complexes with sulfur donor ligands*

The synthesis and some properties of the novel octanuclear mixed-metal complex ion $[Cu_4Mn_4(S^iPr)_{12}S]^{2-}$ possessing a cubane-like Mn_4Cu_4 arrangement has been reported [82]. This anion comprises the first example containing a metal cube with edge-bridging thiolate ligands and an interstitial μ_4-S ion. It was formed during the reaction of $(Me_4N)_2[Mn_2(S^iPr)_6]$ with two equivalents of CuCl in acetonitrile at room temperature and can be isolated as the double salt $(Me_4N)_6[MnCl_4]_2[Cu_4Mn_4(S^iPr)_{12}S]$. This compound can also be obtained by a solvothermal route in which the reaction is run with the reagents in a 1:2.5 molar ratio (Mn:Cu compound) in acetonitrile at 80 °C. An X-ray crystallographic study reveals that the distorted Cu_4Mn_4 cubes comprise two interpenetrating Cu_4 and Mn_4 tetrahedra of slightly different size. At the center of the cube is a μ_4-S atom which binds to each of the manganese atoms with a mean distance of 2.475 Å. The slightly longer edge lengths in the Cu_4 tetrahedra result in mean Cu–S distances of 2.853 Å which are nonbonding. Additionally each metal atom is bound to three outer thiolate ligands generating distorted tetrahedral Mn or distorted trigonal planar Cu coordination sites. The average metal sulfur bonds of 2.506 and 2.200 Å are in the range for tetrahedral Mn and trigonal CuS_3 units. The anion may be viewed in another way as $[Mn_4(SR)_{12}S]^{6-}$ comprising four MnS_4 units sharing a common vertex with its Mn_4S_{13} being a minimal fragment of the cubic closest packed sphalerite-type structure. Magnetic susceptibility measurements have been made in the temperature range 5 to 300 K with the Curie–Weiss law being obeyed between 200 and 300 K, the Mn atoms are antiferromagnetically coupled.

Investigation of the reaction systems Mn^{2+}/S^iPr and Mn^{2+}/Se^iPr has taken place and has resulted in the synthesis and structural properties of the complexes $[Mn_2(SC_3H_7)_6]^{2-}$ (a), $[Mn_2(SCH_3)_6]^{2-}$ (b), $[Mn_2(SeC_3H_7)_6]^{2-}$ (c), $[Mn_4(SC_3H_7)_6Cl_4]^{2-}$ (d) and $[Mn_4(SeC_3H_7)_6Br_4]^{2-}$ (e) [83]. The metal sulfur(selenium) cores of a, b and c consist of two MnX_4 tetrahedra connected via a common edge. Complexes d and e are cage compounds with adamantane-type Mn_4X_6 frameworks in which the tetrahedral coordination sphere of each manganese atom is completed by a terminally bonded halide ion. These complexes have also been characterized by UV–vis spectroscopy.

6.6. Complexes with sulfur and nitrogen donor ligands

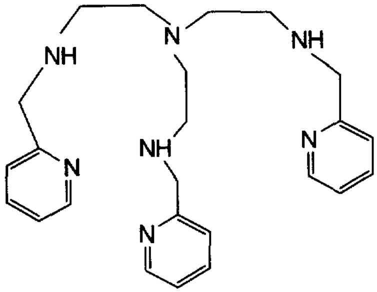
The synthesis and structural characterization of the complex $[Mn([9]\text{-ane}N_2S)_2](ClO_4)_2$ has been reported [84]. It was obtained from the reaction of Mn(II) perchlorate hexahydrate with a methanolic solution of 1-thia-4,7-diazacyclononane ($[9]aneN_2S$) and its structure comprises a distorted octahedral configuration in which all the macrocyclic donor ligands are coordinated to the metal atom. The Mn–N distance is 2.242(7) Å with the Mn–S distance 2.625(3) Å. The magnetic moment at 298 K was 5.82 μ_B indicating an $S=5/2$ configuration. Variable temperature susceptibility showed that the complex was high spin over the whole temperature range with the magnetic moment remaining constant between 80 and 300 K while lowering the temperature to 4.2 K gave an effective magnetic moment of 5.6 μ_B. The solid-state Q-band EPT spectrum gave $g=1.99\pm0.01$, $|D|=0.19\pm0.005\ \text{cm}^{-1}$ and $E/D=0.04\pm0.02$. A comparison of these parameters with those for the analogous hexammine complex $[Mn([9]\text{-ane}N_3)_2](ClO_4)_2$ shows that the thioether complex has a larger axial and smaller rhombic distortion.

The preparation and structure analysis of diaqua[2,6-diacetylpyridine bis(thiosemicarbazone)]manganese(II) diperchlorate has been carried out [85]. The Mn atom is in a distorted pentagonal-bipyramidal environment with two S and three N atoms of the open-chain macrocyclic ligand forming a pentagonal girdle and the oxygen atoms of the water molecules occupying the apical positions. The Mn–N(py) distance is 2.268(3) Å while the Mn–N(imino) distance is 2.634(3) Å. The Mn–S bond is 2.6073(10) Å and there are a number of close contacts in the complex which are suggestive of hydrogen bonding.

6.7. Complexes with nitrogen donor ligands

The synthesis of numerous C-substituted 1,4,7,10,13-pentaazacyclopentadecane, $[15]aneN_5$, ligands and their Mn(II) complexes which are superoxide dismutase mimics has been achieved [86]. Their catalytic superoxide dismutase activity at pH = 7.4 has been studied and the thermodynamic stability of each complex has been determined by potentiometric titration. Kinetic stability as a function of pH was also measured for each complex. Substantial substituent effects were observed with k_{cat} varying in the range $1.4\text{–}9.1\times10^7\ M^{-1}\ s^{-1}$ at pH = 7. Increasing the number of carbon substituents increases the kinetic stability of the complexes while thermodynamic stability was increased to a lesser extent.

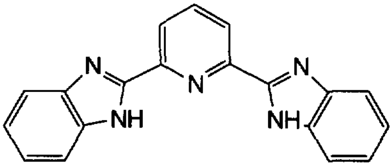
A new Mn(II) complex, Mn(II)–tris[2-[*N*-(2-pyridylmethyl)amino]ethyl]-bishexafluorophosphate, Mn–TPAA, has been synthesized recently [87]. It has been structurally characterized as a seven-coordinate manganese complex with coordination provided by only one ligand, TPPA (**24**), to produce a monocapped antitrigonal prism of [MnN_7] in which the tripodal N atom is bonded to the manganese atom. Three amine nitrogen atoms and three pyridine nitrogen atoms form two equilateral triangles between which the Mn atom is situated. The triangles which are parallel are mutually staggered by $\phi = 54.21°$. The average $Mn–N_{amine}$ distance is 2.28 Å while the average $Mn–N_{pyridine}$ distance is 2.38 Å and the $Mn–N_{tripodal}$ distance is 2.49 Å. The reactivity of this complex with superoxide has been explored indirectly using the xanthine–xanthine oxidase–ferricytochrome *c* assay and directly using electrochemistry and pulse radiolysis. Results from the former study show that this complex inhibits the reduction of ferricytochrome *c* by enzymatic flux of superoxide. The IC_{50} value is 4.3μM. In the electrochemical studies, superoxide was generated *in situ* and the complex was found to induce the one-electron reduction of oxygen. Furthermore, the complex scavenges the superoxide ion. Evidence for this was obtained from pulse radiolysis experiments which show the reaction of Mn–TPAA with superoxide leading to a transient whose difference absorption spectrum is characterized by a peak at 310 nm. Kinetic analysis of this trace shows that the rate constant of the reaction is $(1.05 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$.



(**24**)

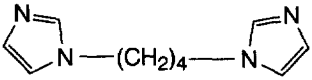
A magnetic study of the compounds $[Mn(4\text{-acpy})_2(N_3)_2]_n$ (acpy = acetylpyridine), $[Mn(Etinc)_2(N_3)_2]_n$ (Etinc = ethyl isonicotinate) and $[Mn(py)_2(N_3)_2]_n$ has been carried out [88]. The acpy and Etinc derivatives were characterized by X-ray crystallography. The former consists of 2-D manganese–azido sheets in which each Mn atom is in a centrosymmetrical octahedral environment. The coordination polyhedron comprises two 4-acpy ligands and four azido ligands in a *trans* coordination with axial elongation along the axis defined by the pyridyl ligand. Each azido ligand acts as a bridge with the next Mn atom in end-to-end coordination. The Etinc derivative also consists of a 2-D compound in which each Mn atom in a *trans* octahedral environment bonded to four azido ligands and two axial pyridyl–(ethyl isonicotinate) ligands. The four azido bridges show two coordination modes: two are coordinated in the end-on mode between two Mn atoms yielding a planar and centrosymmetric Mn_2N_2 unit. Each Mn_2N_2 unit is linked to four neighboring Mn_2N_2 units by four end-to-end azido bridges. The intersheet Mn–Mn distance is close to 15 Å for several manganese atoms. Magnetic studies show ferromagnetic $Mn_2(N_3)_2$ dimeric entities antiferromagnetically linked to four neighboring dimeric moieties through four end-to-end azido bridges leading to an alternate ferromagnetic–antiferromagnetic two-dimensional compound. Molecular orbital calculations (EH) were carried out to gain insight into the superexchange pathway for the manganese 1,3 azido system. The main conclusion from these calculations is that end-to-end bridging between two Mn(II) ions should always be significantly antiferromagnetic.

A communication has appeared describing the synthesis, characterization and superoxide dismutase activity of an Mn(II) complex [89]. Specifically, the potent superoxide dismutase mimic $Mn(HL)_2$, $H_2L = 2,6$-bis(benzimidazol-2-yl)pyridine, (**25**) was obtained by dissolution of the ligand in 100 mL warm methanol followed by the addition of $MnCl_2 \cdot 4H_2O$ and the mixture was refluxed for 10 min. Upon cooling of this solution yellow crystals were recrystallized from methanol–dimethyl sulfoxide–ethyl acetate (1:1:1). An X-ray crystallographic study indicates that the structure is monomeric and there is no chloride present in the manganese coordination sphere. It comprises one Mn atom and two ligands with two solvent molecules, ethyl acetate and water, respectively. The coordination geometry is octahedral and displays considerable distortion. The complex was further characterized by magnetic studies and EPR spectroscopy. Its superoxide dismutase activity was measured using the xanthine–xanthine oxidase–nitro blue tetrazolium method and its IC_{50} value is 0.72 μmol dm^3 which is one of the lowest values reported for a mimic compound.



(**25**)

A report describing how the flexible extended-reach ligand *N*,*N*′-butylenebisimidazole (**26**), bbi, may be used to form not only large metallamacrocyclic rings but also a continuous interpenetrating three-dimensional network has appeared [90]. The reaction between this ligand and hydrated MnX_2 ($X = I$, BF_4) in methanol gave the compound $Mn(bbi)_3(BF_4)_2$ and $Mn(bbi)_3I_2 \cdot H_2O$. The X-band EPR spectra for these compounds consists of a single band at $g_{eff} = 2$ indicative of an Mn(II) ion in an octahedral environment. When $X = Cl$, Br 2:1 complexes were obtained, the X-band spectra revealed pronounced zero-field splitting, a salient feature of tetragonal MnN_4X_2 compounds. From X-ray crystallographic studies it can be seen that each Mn atom is coordinated to six imidazole nitrogen atoms from six different bbi ligands with no statistically significant distortions from octahedral geometry. The structure of the complex essentially consists of two equivalent mutually interpenetrating three-dimensional networks of 44-membered rings. Each bbi ligand has an extended geometry in which the $N(CH_2)_4N$ chain has an all *anti* geometry with its plane steeply inclined by 72° to the imidazole ring planes. Each ligand bridges an adjacent Mn center to form a rhombohedral array with an Mn...Mn edge length of 14.28 Å, the approximate volume of the rhombohedral "box" is 1950 $Å^3$. Rather than forming an open microporous structure the voids are filled by mutual interpenetration of two equivalent three-dimensional frameworks with the vertex of one rhombohedron lying at the body center of another. A pair of BF_4^- anions occupy a cavity created by the region bounded by the all-acute vertices of the two interpenetrating rhombohedra. This cavity likely has the potential to accommodate larger anions and the effects of anion size and organic ligand chain length are currently being explored.

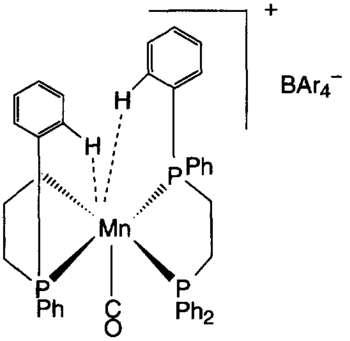


(26)

A communication has appeared describing a synthetic strategy in which six vacant coordination sites about a metal ion could be filled by azido ligands in order to obtain 3-D magnetic systems [91]. The first three-dimensional Mn(II) compound of empirical formula $[N(CH_3)_4][Mn(N_3)_3]$ has been obtained. Its crystal structure has been obtained and shows that the azido groups act as end-to-end bridging ligands between the Mn centers forming a three-dimensional network with each Mn atom possessing a slightly distorted octahedral coordination sphere. The tetramethylammonium cations are located in the cavities of the Mn(II)–azido sublattice. The Mn...Mn distance is 6.4 Å. This compound was found to undergo a reversible phase transformation at 303 K. The pseudo-cubic high-temperature phase at 310 K has a cell length of 6.6446(4) Å, the crystal structure of this phase is presently under investigation. The compound has been further characterized by EPR and magnetic susceptibility measurements.

6.8. Complexes with phosphorus donor ligands

A new 16-electron precursor $[Mn(CO)(dppe)_2]BAr'$, $BAr' = B[C_6H_3(3,5\text{-}CF_3)_2]_4$, has been synthesized [92]. It was formed in the reaction of $Mn(CO)(dppe)_2Br$ with the sodium salt of the large non-coordinating anion NaBAr′ in dichloromethane followed by filtration to remove NaBr. The deep blue complex is extremely moisture and air sensitive, is soluble in aromatic solvents and dichloromethane but is insoluble in hydrocarbons and crystallizes from toluene as a solvate containing 0.7 toluene after drying *in vacuo*. It was characterized by X-ray crystallography and is formally a five-coordinate square-pyramidal cation. A salient feature is the presence of two agostic hydrogen interactions from *ortho*-hydrogen atoms of the phenyl ring of mutually *trans* phosphines (**27**). The Mn...H distances of 2.89(6) and 2.98(6) Å are long. This complex was fully characterized by ^1H and ^{31}P NMR spectroscopies. When a solution containing the complex is placed under H_2 the complex $[Mn(H_2)(CO)(dppe)_2]BAr'$ which is light yellow is obtained. The hydrogen is quite labile and dissociates readily when the hydrogen atmosphere is removed or the complex is warmed. The H–H distance was determined by solid-state NMR measurements to be 0.89(2) Å. A nitrogen complex was obtained by placing CH_2Cl_2 solutions of [Mn(CO)(dppe)$_2$]BAr′ under N_2 at −78 °C. Addition of the nitrogen caused the blue solution to turn yellow which upon warming to room temperature turned blue-green. A ^{15}N NMR spectroscopic study was carried out to determine whether the nitrogen was bridging or terminal and results were consistent with a terminal orientation. This was further confirmed with IR spectroscopy of solid mulls.



(27)

Cyanomanganese ligands have been reacted with dirhodium triazenide fragments to form novel tri- and tetra-metallic complexes containing two or three redox-active sites [93]. The oxidation state of the dirhodium core can be varied in a systematic fashion and the order of oxidation of the various sites can be controlled by varying their ancillary ligands and their arrangement at the Mn centers.

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